LOW FREQUENCY INFRARED AND OTHER STUDIES OF COORDINATION COMPLEXES

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ABSTRACT

This thesis is divided into two main sections. Section I is concerned with oxygen and sulphur ligand complexes of the divalent first row transition metals, and oxygen and nitrogen ligand complexes of the Group VB trihalides are described in Section II.

Section I

(1) The preparation of new tertiary phosphine sulphide and arsine sulphide complexes of cobalt (II) is reported. Comparative spectral and magnetic data are presented for the tetrahedral oxo- and thio-ligand complexes of the types $[CoL_4](ClO_4)_2$ and CoL_2X_2 (X = Cl, Br and I). (L = Me_3PO and Me_3PS; Me_3AsO and Me_3AsS). In the perchlorate complexes corresponding oxo- and thio-ligands produce similar ligand field splitting energies, but lower β values of the sulphides and higher intensities of their spectral bands point to their greater covalent character. The considerably lower magnetic moments of $[CoL_4](ClO_4)_2$ thio-complexes as compared with their oxo-analogues is further evidence for differences in metal-oxygen and metal-sulphur bonding. Electronic spectra for the $[CoL_4](ClO_4)_2$ complexes have been compared with the spectra of related tetrahedral cobalt (II)

complexes. The $^4A_2 \rightarrow {}^4T_1(P)$ transition band shapes and intensity distributions are virtually identical for both the phosphine and arsine sulphides. In contrast the characteristic profiles produced by phosphine oxides are different from those produced by arsine oxides. Metal-ligand vibrations have been assigned for cobalt and corresponding zinc complexes.

(2) Spectral and magnetic results show that trimethylarsine sulphide continues to give tetrahedral $[M(Me_3AsS)_4](ClO_4)_2$ and $M(Me_3AsS)_2X_2$ (X = Cl, Br) complexes with iron (II) and nickel (II). The low β value and magnetic moment of $[Ni(Me_3ASS)_4](ClO_4)_2$ again demonstrates the high metal-ligand covalency produced by thio-ligands. Metal-ligand vibrations fall in the same frequency range as observed for cobalt (II) complexes.

By contrast trimethylarsine oxide reacts with the dihalides of iron, cobalt and nickel to give bridged octahedral $M(Me_3AsO)_2X_2$ (X = Cl, Br) complexes thus providing an example of tetrahedral bridged octahedral isomerism involving oxo-ligands. Their structures have been elucidated using infra-red and electronic spectral, and magnetic data. The low As - O stretching frequencies

suggest that polymerisation is being achieved via oxo- rather than halogen bridges. Further evidence is obtained from the infra-red spectra of the analogous $M(Me_3AsO)_2(NCS)_2$ thiocyanate complexes.

(3) The preparation of high-spin five-co-ordinate $[ML_5]^{2+}$ and $[ML_4(ClO_4)]^{+}$ complexes with trimethylarsine oxide is described for a number of first-row, divalent, transition metal ions. The electronic spectra of these complexes more closely resemble the spectra obtained for other complexes known, from X-ray analysis, to have a basically square pyramidal structure rather than those of the trigonal bipyramidal class. Five co-ordination is considered to be stabilised by the steric requirements of the ligand. Metal-ligand stretching vibrations are assigned and their frequencies compared with values for related tetrahedral complexes.

Section II

Metal-ligand stretching frequencies have been assigned for MX_3 dipy and MX_3L_2 (L = py, pyO and Ph_3AsO) complexes of arsenic, antimony and bismuth. For the arsenic and antimony MX_3L_2 compounds, $\nu(M - L)$ values fall in the same region as for the corresponding

germanium and tin, MX_4L_2 compounds. However, ν(Sb - X) values are significantly lower than ν(Sn - X).

Terpyridyl complexes are varied. Their compositions and constitutions were elucidated by spectral and conductivity studies. Antimony complexes are formulated as $[SbX_2 terpy]_2^+ SbX_5^{2-}$ and arsenic complexes as $[AsCl_2 terpy]^+ AsCl_4^-$ and $[AsBr_2 terpy]^+ Br^-$. The bismuth complex $[BiCl_3 terpy]$ is non-ionic.

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SECTION II

GENERAL INTRODUCTION

The present work is primarily a comparative study involving a variety of coordination compounds which all can be regarded as being of the general type MX_aL_b, where M is a central metal ion, X a coordinated or uncoordinated anion and L a neutral ligand. Examples are $NiCl_2(Me_3AsS)_2$, $SbBr_3(pyO)_2$ and $Mn(ClO_4)_2(Me_3AsO)_5$. In a given series either M, X or L have been systematically varied and the resultant changes in stereochemistry and the nature of the M-L bond investigated. A comparison of the effects of changing the L donor atom from oxygen to sulphur, using trimethylarsine oxide and sulphide, and related ligand complexes of the divalent first row transition elements has been made (Section I). The effects of varying M and X, using some Group VB trihalide complexes has also been studied (Section II) and comparisons made with related Group IVB and transition element complexes.

The present work involved the use of a number of physical methods. Electronic spectra have been used to distinguish between four, five and six-coordinate complexes and also to give information about the metal-ligand bond. For example the Racah B values were

found to be significantly lower for the tetrahedral cobalt(II) thio-complexes than for their oxo-analogues demonstrating the greater metal-ligand covalency produced by the thio-ligands.

In certain cases, such as the nickel and cobalt halide complexes, magnetic moments distinguish between octahedral and tetrahedral stereochemistries, thus complementing spectral information. Electron delocalisation may also effect magnetic moments, as was observed for the tetrahedral cobalt(II) thio-complexes.

In cases where electronic spectra and magnetic measurements fail to distinguish between possible coordination numbers, X-ray powder photographs may establish isomorphism with a complex of known stereochemistry.

In the region above 500 cm^{-1}, infrared spectroscopy has been used to establish ligand coordination. Certain changes in ligand frequencies, such as a decrease in the arsenic-oxygen stretching frequency for arsine oxide complexes, are indicative of complex formation, and may also be characteristic of the coordination environment.

Finally, extensive use of low frequency infrared

spectroscopy has been made in the present work. This technique is being used increasingly in the study of inorganic compounds[1,2,3]. Metal-ligand and metal-halogen stretching frequencies, which occur in the region below 500 cm^{-1}, frequently give information about the nature of bonding and the structure of complexes. Although such absorptions have been assigned as ν(M-O), ν(M-N) or ν(M-Cl) for example, it is realised that these may not be pure stretching modes but may involve bending components or coupling with ligand modes. However in a closely related series of complexes the degree of mixing of vibrations will probably be approximately constant, and changes in metal-ligand stretching frequencies can therefore be correlated with changes in metal-ligand bond stretching force constants. Metal-halogen and metal-ligand frequencies are often characteristic of structure and stoichiometry. For example the differentiation of the tetrahedral and bridged octahedral isomers of the formula MX_2L_2 has been accomplished.

Far infrared spectroscopy is of particular value when neither electronic spectra nor magnetic measurements give structural information, as is the case for

complexes of metal ions involving filled d shells. However, whenever possible, low frequency infrared spectroscopy has been employed in conjunction with the other physical methods to provide the fullest information about the bonding and structures of the coordination complexes.

SECTION I

TRIMETHYLARSINE OXIDE, TRIMETHYLARSINE SULPHIDE AND RELATED LIGAND COMPLEXES OF THE DIVALENT FIRST ROW TRANSITION ELEMENTS

INTRODUCTION

In this section a comparison of the effects produced by related oxo- and thio-ligands has been made. Such ligands are often mutually exclusive in their reactivity; oxo-ligands generally forming stable complexes with "class a" or "hard" metal ions, and thio-ligands forming stable complexes with "class b" or "soft" metal ions[4,5]. Therefore in order to obtain comparative data, the divalent metal ions of manganese, iron, cobalt, nickel, copper and zinc, which lie on the boundary between the "class a" and "class b" acceptors, were chosen for study. To avoid any possible complications arising from chelation, only monodentate ligands have been considered, those used being of the type R_3ZY (where R = Ph, Me; Z = P,As; and Y = O,S). Several other systems were investigated but found to be unsuitable. (Appendix I).

Whereas the tertiary phosphine and arsine oxides (R_3PO and R_3AsO) are known to react readily with the divalent ions of the first row transition elements[6-9] stable complexes of the corresponding sulphides (R_3PS and R_3AsS) have been reported mainly with typical "class b" elements[10-16]. Previous workers[13-16]

have found no evidence for complex formation between the sulphides Me_3PS, Ph_3PS and Ph_3AsS, and the dihalides of cobalt and nickel. However, the phosphine sulphide complexes[11,17] ZnL_2X_2 (where L = Me_3PS, Ph_3PS and Ph_3AsS) and $[Zn(Me_3PS)_4](ClO_4)_2$, and a triethylarsine sulphide complex[18] $Co(Et_3AsS)_2Cl_2$ have been described briefly. No trimethylarsine sulphide, Me_3AsS, complexes have been reported previously.

In the present work structurally analogous oxo- and thio-ligand complexes have been obtained thus facilitating a direct comparison of the effects produced by these ligands. Spectroscopic and magnetic properties of the corresponding pairs of tetrahedral complexes formed between cobalt(II) and the ligands Me_3PO and Me_3PS, Me_3AsO and Me_3AsS, and Ph_3AsO and Ph_3AsS have been compared (Chapter 1). (Results in Chapter 1 were jointly analysed with Miss S.H. Hunter, who prepared the tetrahedral cobalt(II) oxo-ligand complexes.) The work was then extended (Chapter 2) to include an investigation of the coordination properties of divalent manganese, iron, nickel and copper towards trimethylarsine oxide and sulphide. These ligands were chosen to represent the Me_3ZY class,

since preliminary investigations indicated that their complexes were more readily isolated and less hygroscopic than the corresponding Me_3PO and Me_3PS compounds. It was found that although both the oxo- and thio-complexes have the same general formulae, $ML_4(ClO_4)_2$ and ML_2X_2, they are structurally different. Finally the complexes of trimethylarsine oxide and the divalent perchlorates were investigated in more detail because they were found to be five-coordinate (Chapter 3).

Although the metal-ligand stretching frequencies for oxo-ligand complexes are well established[9,19,20], less is known about the corresponding thio-frequencies[1]. Mainly bidentate sulphur ligand complexes have been investigated[1], and so the identification of the ν(M-S) mode for a series of monodentate sulphur ligand complexes was of interest, the usual difficulties and uncertainties associated with chelate ligands being avoided. The simplicity of the spectra of the Me_3ZY ligands makes the infrared spectra of their complexes particularly attractive for study.

CHAPTER 1

TETRAHEDRAL COBALT(II) COMPLEXES

INTRODUCTION

In contrast to earlier reports[13,14] it is found that both tertiary phosphine and arsine sulphides react with cobalt(II) salts. With trimethylphosphine and arsine sulphides a full range of tetrahedral $[CoL_4](ClO_4)_2$ and CoL_2X_2 (where L = Me_3PS and Me_3AsS; X = Cl, Br I and NCS) compounds were obtained. Triphenylarsine sulphide, Ph_3AsS, also reacts, although only impure products could be isolated (p.115). There was no definite indication of complex formation between triphenylphosphine sulphide, Ph_3PS, and cobalt(II). Since Me_3PO, Me_3AsO and Ph_3AsO all react with cobalt perchlorate and halides to give the corresponding tetrahedral oxo-complexes $[CoL_4](ClO_4)_2$ and CoL_2X_2,[8,19,21] an opportunity is provided to make a direct comparison of the effects produced by monodentate oxo- and thio-ligands. The complexes studied are listed in Table 1. Only in the cobalt iodide and thiocyanate complexes of Me_3AsO and Me_3AsS are there significant structural differences. Trimethylarsine sulphide gives the tetrahedral $Co(Me_3AsS)_2I_2$ complex while trimethylarsine oxide gives an ionised complex $[Co(Me_3AsO)_4]I_2$, with

a tetrahedral cation. $Co(Me_3AsO)_2(NCS)_2$ is six-coordinate through bridging in the crystalline state, (see Chapter 2), in contrast to $Co(Me_3AsS)_2(NCS)_2$ which is tetrahedral.

Examples of corresponding pairs of stable complexes with monodentate oxo- and thio-ligands, such as those studied in the present work, are not common. Both hexamethylphosphoramide, $(Me_2N)_3PO$[22,23] and tris(dimethylamino)phosphine sulphide, $(Me_2N)_3PS$ [24] have been reported to give tetrahedral $[CoL_4](ClO_4)_2$ and CoL_2X_2 complexes. Other oxo-thio pairs of cobalt(II) complexes involve the $\geq C=O$ and $\geq C=S$ donor groups, but comparisons obtainable from such complexes appear to be limited. Dimethylacetamide (dma) [25,26] and dimethylthioacetamide (dmta) [27] give a full range of tetrahedral $[CoL_4](ClO_4)_2$ and CoL_2X_2 complexes. However, it has been suggested from spectroscopic data, that although the oxygen is acting as the donor atom in the $[Co(dma)_4](ClO_4)_2$ complex, the nitrogen may also be weakly bonded[25]. A similar series of complexes can also be obtained with tetramethylurea (tmu) [28,29] and tetramethylthiourea (tmtu) [29,30], but the electronic spectra of the thio-complexes have not been reported and since the tetramethylurea

complexes are very hygroscopic, difficulty was found in obtaining reliable magnetic measurements from $[Co(tmu)_4](ClO_4)_2$[28].

Corresponding pairs of oxo- and thio-ligand complexes with metal atoms having a d^0 or d^{10} configuration are more common. Triphenylarsine oxide[9] and sulphide[17] both react with zinc halides giving ZnL_2X_2 complexes. Tin tetrahalides react with Me_3PO[19] and Me_3PS[31] to give $SnX_4{:}2L$ complexes, which are presumably octahedral. With mercuric chloride, 1:1 adducts are formed with Ph_3AsO[32] and Ph_3AsS[14]; however, the oxo-complex is dimeric with bridging arsine oxide ligands[33], whereas the structure of the thio-complex is not known. Ethers and thioethers react with the trihalides of aluminium and gallium[34] and with the pentachlorides of niobium and tantalum[35], giving MX_3L and MCl_5L complexes respectively. Such corresponding pairs of oxo- and thio-ligand complexes have the same stoichiometry, but often no evidence is presented to indicate that the compounds are structurally similar.

In this chapter a direct comparison of the effects produced by corresponding oxo- and thio-ligands has been made using the structurally analagous

pairs of tetrahedral $[CoL_4](ClO_4)_2$ and CoL_2X_2 complexes (where L = Me_3PO and Me_3PS, Me_3AsO and Me_3AsS and Ph_3AsO and Ph_3AsS). Zinc complexes have been included as reference compounds.

TABLE 1

Tetrahedral Cobalt(II) Complexes Studied in Chapter 1

Ligand	Complexes
Me_3PO	$[CoL_4](ClO_4)_2$
Me_3PS	CoL_2X_2 (X = Cl, Br, I)
Me_3AsO	$[CoL_4](ClO_4)_2$ CoL_2X_2 (X = Cl,Br) $[CoL_4]I_2$ $CoL_2(NCS)_2$ [a]
Me_3AsS	$[CoL_4](ClO_4)_2$ CoL_2X_2 (X = Cl,Br,I) $CoL_2(NCS)_2$
Ph_3PS	No indication of complex formation
Ph_3AsO [b]	$[CoL_4](ClO_4)_2$
Ph_3AsS [c]	CoL_2Br_2

[a] Octahedral complex (see Chapter 2)

[b] Ph_3AsO complexes described in ref. 8

[c] Only impure products could be isolated (p.115)

TABLE 2

d values for X-ray powder lines of ML_2X_2 tetrahedral complexes[a]

$Co(Me_3AsO)_2Cl_2$	7.86m	6.51s	b	5.24s	4.76m	4.07m	3.82s	3.06s
$Zn(Me_3AsO)_2Cl_2$	7.98m	6.53s	b	5.26s	4.93m	4.08m	3.83s	3.10s
$Co(Me_3AsO)_2Br_2$	8.11m	6.65s	b	5.34s	5.01m	4.17m	3.89s	3.14s
$Co(Me_3AsS)_2Cl_2$	b	6.68s	5.89m	5.20s	b	4.02m	3.88s	3.10s
$Zn(Me_3AsS)_2Cl_2$	b	6.71s	5.91m	5.22s	b	4.05m	3.90s	3.11s
$Co(Me_3AsS)_2Br_2$	b	6.84s	6.02m	5.31s	b	4.11m	3.95s	3.16s

[a] s = strong, m = medium

[b] line not observed.

RESULTS AND DISCUSSION

The new thio-complexes were obtained from hot acetone or ethanol solutions of the ligand and the metal salt (p.100). For the Me_3AsS complexes, use of the anhydrous salt was found unnecessary. The addition of ethylorthoformate considerably increased the yields of the Me_3PS complexes, and was essential for the isolation of Ph_3AsS complexes with cobalt(II). The dehydration of the metal ions by ethylorthoformate (p.125) facilitates the formation of the sulphide complexes. The tetrahedral cobalt oxo-complexes were prepared by Miss S.H. Hunter, and the corresponding zinc oxo-complexes were isolated from ethanol solutions of the ligand and metal salt.

X-ray powder photographs show that groups of isomorphous compounds are:

(i) CoL_2Cl_2, CoL_2Br_2, ZnL_2Cl_2 and ZnL_2Br_2 where L = Me_3PO and Me_3AsO.

(ii) CoL_2Cl_2, CoL_2Br_2, CoL_2I_2, ZnL_2Cl_2 and ZnL_2Br_2 where L = Me_3PS and Me_3AsS.

(iii) $[CoL_4](ClO_4)_2$ and $[ZnL_4](ClO_4)_2$ where L =

Me_3PO and Me_3AsO.

(iv) $[CoL_4](ClO_4)_2$ and $[ZnL_4](ClO_4)_2$ where L = Me_3PS and Me_3AsS.

(v) $[CoL_4](ClO_4)_2$ and $[ZnL_4](ClO_4)_2$ where L = Ph_3AsS.

The similarity in the diameters of the stronger lines in the photographs of the group (i) and (ii) compounds (Table 2) suggests that they are of closely similar structure.

Electronic Spectra

The electronic spectra of the thio-complexes (Table 3) are characteristic of tetrahedrally coordinated cobalt(II)[36,38]. The positions of the bands are similar in the reflectance and solution spectra and generally the molar absorbances of the solutions obey Beer's Law. However, for the relatively unstable complexes, $[Co(Me_3PS)_4](ClO_4)_2$, $[Co(Ph_3AsS)_4](ClO_4)_2$ and $Co(Ph_3AsS)_2Br_2$, which show ligand dissociation in solution, free ligand was added to restore band intensities to their maximum values. Molar conductivities of the $Co(Me_3AsS)_2X_2$ compounds in nitrobenzene are all low (for X = Cl, Br and I, $\Lambda_m < 2$; for X =

TABLE 3

Electronic Spectral Data for Tetrahedral Cobalt(II) Complexes (cm^{-1})[a]

Compound	State	ν_3			ν_2		
$[Co(Me_3PS)_4](ClO_4)_2$	nitromethane[b]	15,380(526)	14,490(705)	13,510(650)	7,350(143)	6,000(143)	
	solid	15,400	14,800	13,600	7,350	5,950	
$Co(Me_3PS)_2Cl_2$	dichloromethane	16,560(436)	15,170(436)	13,330(457)	6,900(sh)	5,210(123)	
	solid	16,100	14,800	13,600	6,600	5,250	
$Co(Me_3PS)_2Br_2$	dichloromethane	15,850(468)	14,730(506)	13,230(540)	6,620(sh)	5,000(115)	
	solid	15,600	14,200	13,500	6,500	4,900	
$Co(Me_3PS)_2I_2$	dichloromethane	14,840(575)	13,870(749)	12,820(871)	6,350(117)	4,940(117)	
	solid	14,800	13,700	12,800	6,100	4,800	
$[Co(Me_3AsS)_4](ClO_4)_2$	nitromethane	15,290(531)	14,410(778)	13,400(717)	7,670(163)	6,230(161)	
	solid	15,300	14,500	13,400	7,700	6,100	
$Co(Me_3AsS)_2Cl_2$	dichloromethane	16,290(448)	15,040(444)	13,320(416)	6,990(sh)	5,280(129)	
	solid	16,000	14,800	13,600	6,700	5,400	
$Co(Me_3AsS)_2Br_2$	dichloromethane	15,700(512)	14,730(545)	13,390(551)	6,670(sh)	5,100(126)	
	solid	15,400	14,300	13,300	6,650	5,200	
$Co(Me_3AsS)_2I_2$	dichloromethane	14,860(991)	13,850(1210)	12,820(1267)	6,580(120)	4,980(123)	
	solid	14,800	13,800	12,700	6,200	4,900	
$Co(Me_3AsS)_2(NCS)_2$	dichloromethane	16,780(526)	15,360(670)	13,950(757)	7,700(sh)	7,240(204)	6,700(sh)
	solid	17,300	15,700	13,800	8,100	7,350	6,450
$[Co(Ph_3AsS)_4](ClO_4)_2$	nitromethane[b]	15,150	14,370	13,890	7,840	5,920	
	solid	15,100	14,350	13,900	7,800	5,900	
$Co(Ph_3AsS)_2Br_2$	dichloromethane[b]	15,820	14,470	13,090	6,600(sh)	4,960	
	solid	15,700	14,600	13,300	6,600	4,700	

[a] For corresponding oxo-complexes see refs 21,37; molar extinction coefficients in parentheses.

[b] Plus excess ligand.

TABLE 4a

Electronic Spectral Parameters for Tetrahedral $[CoL_4](ClO_4)_2$ Complexes[a]

Compound	ν_3[b] (cm^{-1})	ν_2[b] (cm^{-1})	Δ[c] (cm^{-1})	B' (cm^{-1})	β[d]	f[e] (ν_3) ($\times 10^3$)
$[Co(Me_3PO)_4](ClO_4)_2$	16,890	6,600	3,800	805	0.83	3.22
$[Co(Me_3PS)_4](ClO_4)_2$	14,400	6,680	3,890	627	0.65	8.59
$[Co(Me_3AsO)_4](ClO_4)_2$	16,810	6,900	3,980	784	0.81	3.78
$[Co(Me_3AsS)_4](ClO_4)_2$	14,280	6,950	4,070	601	0.62	9.62
$[Co(Ph_3AsO)_4](ClO_4)_2$	16,600	6,650	3,830	784	0.81	-
$[Co(Ph_3AsS)_4](ClO_4)_2$	14,430	6,940	4,060	613	0.63	-

[a] Oxo-complexes from refs 21,37

[b] Evaluated from the centre of gravity of the intensities

[c] Calculated by the methods described in ref.36; considered reliable to $\pm$ 150cm^{-1}

[d] $\beta = B'/967$; reliable to $\pm$ 0.02

[e] Oscillator strength, f, evaluated graphically.

TABLE 4b

Electronic Spectral Parameters for Tetrahedral CoL_2X_2 Complexes[a]

Compound	ν_3[b] (cm^{-1})	ν_2[b] (cm^{-1})	Δ[c] (cm^{-1})	B' (cm^{-1})	β[d]	f[e] (ν_3) ($\times 10^3$)
$Co(Me_3PO)_2Cl_2$	15,750	6,440	3,730	735	0.76	4.54
$Co(Me_3PO)_2Br_2$	15,590	6,230	3,590	737	0.76	4.63
$Co(Me_3PO)_2I_2$	15,300	6,000	3,450	730	0.75	6.28
$Co(Me_3PS)_2Cl_2$	14,990	5,810	3,340	719	0.74	6.80
$Co(Me_3PS)_2Br_2$	14,540	5,700	3,280	693	0.72	7.42
$Co(Me_3PS)_2I_2$	13,710	5,650	3,260	639	0.66	9.18
$Co(Me_3AsO)_2Cl_2$	15,880	6,660	3,840	735	0.76	4.06
$Co(Me_3AsO)_2Br_2$	15,600	6,340	3,650	732	0.75	4.78
$[Co(Me_3AsO)_4]I_2$	15,900	6,700	3,880	730	0.76	5.64
$Co(Me_3AsS)_2Cl_2$	14,920	5,900	3,390	710	0.73	7.15
$Co(Me_3AsS)_2Br_2$	14,580	5,750	3,310	693	0.72	7.67
$Co(Me_3AsS)_2I_2$	13,760	5,770	3,340	634	0.66	13,98
$Co(Me_3AsS)_2(NCS)_2$	15,200	7,220	4,220	651	0.67	11.61
$Co(Ph_3AsO)_2Br_2$	15,000	5,670	3,250	727	0.75	-
$Co(Ph_3AsS)_2Br_2$	14,510	5,600	3,220	696	0.72	-

[a] Oxo-complexes from refs 21,37

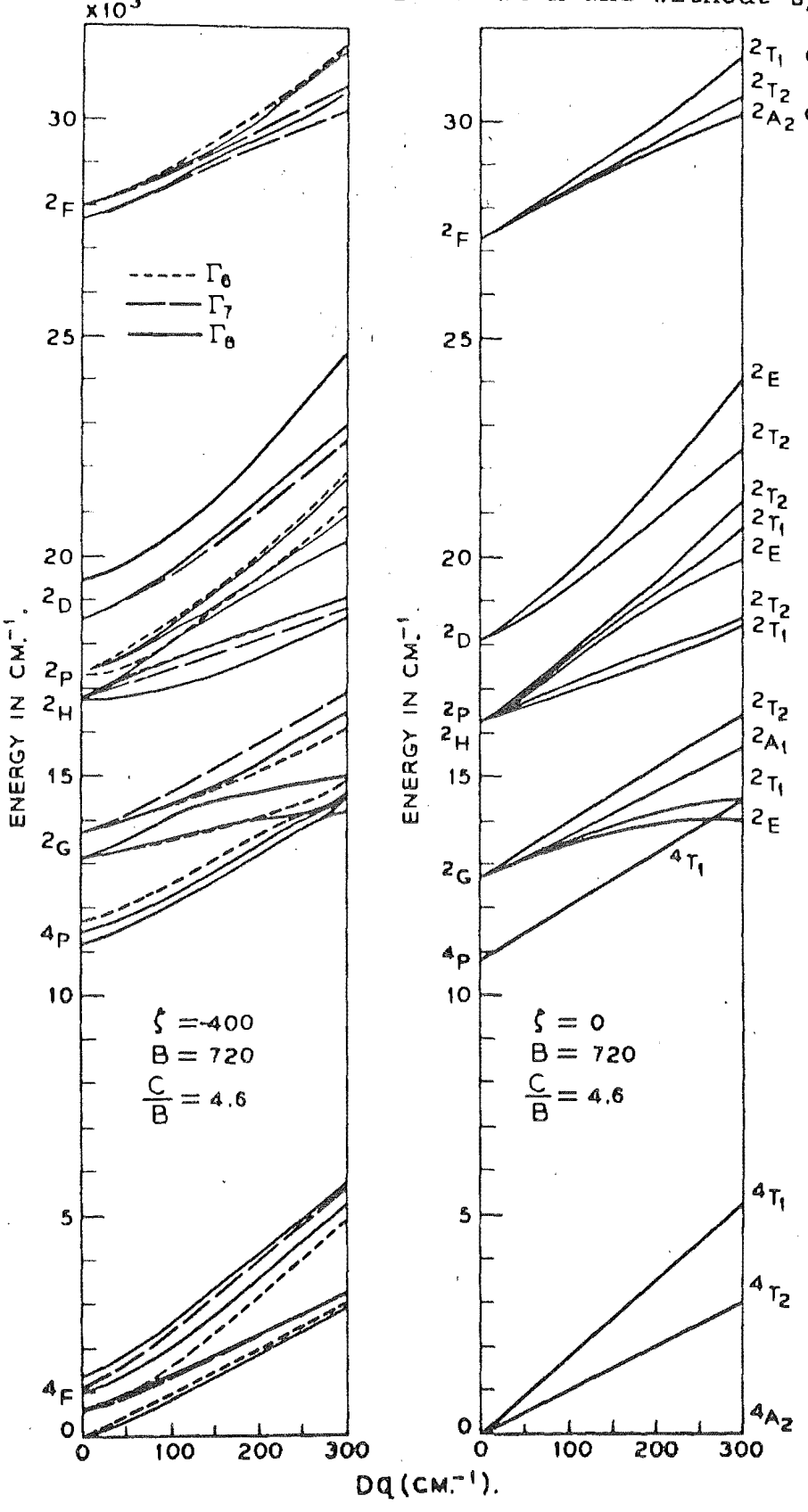
[b] Evaluated from the centre of gravity of the intensities

[c] Calculated by the methods described in ref.36; considered reliable to $\pm$ 150cm^{-1}.

[d] $\beta = B'/967$; reliable to $\pm$ 0.02

[e] Oscillator strength, f, evaluated graphically.

FIGURE 1. Calculated energy levels for cobalt(II) in a tetrahedral field with and without spin-orbit coupling. (ref. 38)



NCS, Λ_m = 3.2 cm^2 ohm^{-1} $mole^{-1}$) thus excluding alternative ionic formulations. The electronic spectra of the tetrahedral oxo-complexes of cobalt(II) are reported in detail elsewhere[21,37].

A consideration of the energy level diagram (Figure 1) for tetrahedral cobalt(II) predicts three spin-allowed electronic transitions from the $^4A_2$ ground state. The first, $^4A_2 \longrightarrow {}^4T_2$, ν_1, would be expected to occur in the 5000 - 3000 cm^{-1} region but although searched for was not observed. The structured bands in the regions 8000 - 4500 cm^{-1} and 18,000 - 12,500 cm^{-1} have been assigned to the $^4A_2 \longrightarrow {}^4T_1(F)$, ν_2 and $^4A_2 \longrightarrow {}^4T_1(P)$, ν_3 transitions respectively[36,38].

Spectral Parameters

Single energy values for the ν_2 and ν_3 bands were evaluated from the centre of gravity of the total absorptions. The spectral parameters Δ and B' were then calculated from the energies of ν_2 and ν_3 using the equations [36] derived from the matrices of Tanabe and Sugano[39] (Appendix II). The nephelauxetic parameter, β, is the ratio B' to B, the free ion value. Since the spectra usually involve broad bands,

assignment of single energy values for ν_2 and ν_3 is somewhat arbitrary. Thus too much emphasis should not be placed on small differences in the parameters. The oscillator strengths of the ν_3 bands were evaluated graphically. The derived spectral data are given in Table 4 along with the values for the corresponding oxo-complexes.

The ligand field splitting energies Δ, for the corresponding pairs of $[CoL_4](ClO_4)_2$ complexes (where L = Me_3PO and Me_3PS; L = Me_3AsO and Me_3AsS) are remarkably similar. However the values of the Racah interelectronic repulsion integrals, B', are significantly lower for the thio-complexes indicating greater covalency. The decreased β (B'/B) values are considered to be caused by charge transfer from the ligands to the central metal atom and a spreading of the partly filled d shell over the ligands, thereby increasing the mean orbital radii, the two effects being mutually reinforcing[36,40]. As further evidence of covalency it is found that in the $Co(Me_3PS)_2X_2$ and $Co(Me_3AsS)_2X_2$ series only the iodides give β approaching the low values obtained for the $[CoL_4](ClO_4)_2$ thio-complexes. Since calculations provide evidence that the intensities of the spectral

bands are direct functions of the mixing of ligand and metal d orbitals[41], the higher oscillator strengths of the bands in the thio-complexes again indicate greater covalency in the metal-ligand bond. The fact that the corresponding pairs of ligands, Me_3PO and Me_3PS, or Me_3AsO and Me_3AsS, produce similar Δ values, must arise fortuitously from compensating effects of permanent polarity and polarisability, the polarisability of the thio-ligands being considerably greater. The recent preparation of cobalt(II) complexes of tris(dimethylamino)phosphine sulphide, $(Me_2N)_3PS$[24] allows an extension of the oxo-thio comparison. The ligand field splitting energies produced by this thio-ligand[24] (Δ = 3620 cm^{-1}) and its oxo-analogue[22] (Δ = 3640 cm^{-1}) in their $[CoL_4](ClO_4)_2$ complexes are also remarkably similar.

With Δ values 3800, 3830, 3890, 3920, 3980, 4060, 4070, 4150 and 4250 cm^{-1} respectively trimethylphosphine oxide, triphenylarsine oxide, trimethylphosphine sulphide, azide[36], trimethylarsine oxide, triphenylarsine sulphide, trimethylarsine sulphide, cyanate[36] and thiourea[42] fall approximately in this sequence in the spectrochemical series. The low β values observed for the sulphides are characteristic for

cobalt(II) in a tetrahedral field of sulphur atoms (Table 5). A low β value (0.60) is also found for cobalt(II) doped into a zinc selenide lattice[45]. Investigation of the reactions of trimethylarsine and trimethylphosphine selenides towards cobalt(II) would therefore be of interest.

It appears that corresponding oxo- and thio-ligands may produce similar ligand field splitting energies in other systems, as for example in octahedral $[NiL_6](ClO_4)_2$ complexes. Although exactly analogous pairs of complexes have not been investigated, the urea (O bonded) and ethylenethiourea (S bonded) nickel(II) perchlorate complexes are known. The Δ values are 8060 and 8000 cm^{-1} and the β values 0.87 and 0.54 respectively[46,47] (B for free ion = 1056 cm^{-1}).

Magnetic Susceptibilities

The magnetic susceptibilities of the complexes, corrected for diamagnetism and temperature independent paramagnetism are given in Table 6. The latter was calculated from the expression $2.09/\Delta$[36]. Precision was such that reproducibility of the values is $\pm$ 0.04 B.M.

TABLE 5

Spectral Parameters for $[CoL_4]^{2+}$ Thio-complexes

L	$\Delta(cm^{-1})$	β
Me_3PS	3890	0.65
Me_3AsS	4070	0.62
Ph_3AsS	4060	0.63
TDPS [a]	3620	0.66
Tu [b]	4250	0.62
etu [c]	3780	0.67
dmta [d]	3870	0.67
tcl [e]	3910	0.64

[a] Tris(dimethylamino)phosphine sulphide (ref. 24)

[b] Thiourea (ref. 42)

[c] Ethylenethiourea (ref. 43)

[d] Dimethylthioacetamide (ref.27)

[e] ε-Thiocaprolactam (ref.44).

TABLE 6

Magnetic Data for Tetrahedral Cobalt(II) Complexes[a]

Compound	$\chi_m(X10^3)$ (cgsu)	$\chi_m^{corr}(X10^3)$ (cgsu)[b]	μ c (B.M.)	
$[Co(Me_3PS)_4](ClO_4)_2$	8.00	7.87	4.31	(4.56)
$Co(Me_3PS)_2Cl_2$	8.32	7.91	4.32	(4.34)
$Co(Me_3PS)_2Br_2$	8.64	8.23	4.41	(4.46)
$Co(Me_3PS)_2I_2$	8.65	8.27	4.42	(4.46)
$[Co(Me_3AsS)_4](ClO_4)_2$	8.23	8.19	4.46[d]	(4.66)
$Co(Me_3AsS)_2Cl_2$	8.26	7.87	4.31	(4.42)
$Co(Me_3AsS)_2Br_2$	8.40	7.97	4.34	(4.46)

[a] At 293°K

[b] Corrected for diamagnetism and temperature independent paramagnetism.

[c] Values for corresponding oxo-complexes in parentheses; from refs. 21, 37.

[d] $\Theta = -4^o$.

For tetrahedral cobalt(II) higher energy triplet states are mixed into the $^4A_2$ ground state under the action of spin-orbit coupling. A certain amount of orbital angular momentum is introduced into the ground state and thus, an orbital contribution to the magnetic moment[48,49]. The magnitude of this contribution is given by[48]

$$\mu = 3.88(1 - \frac{4\lambda'}{\Delta})$$

where λ' (a negative number) is the spin-orbit coupling constant in the complexed cobalt(II) ion. In discussion of the increments in the magnetic moments above the spin only value, attention has generally been focussed on the variations in Δ produced by different ligands[38,48,50]. In the present case, the closely similar Δ values for the ligands in the corresponding pairs of perchlorate complexes, allows the differences in magnetic moments to be interpreted in terms of spin-orbit coupling. For the $[CoL_4](ClO_4)_2$ compounds μ = 4.56 and 4.31 B.M. for L = Me_3PO and Me_3PS and μ = 4.66 and 4.43 B.M. for L = Me_3AsO and Me_3AsS respectively. Thus the lower magnetic moments of the thio-complexes appear to arise primarily from decreased spin-orbit coupling. The reduction in λ has been related to charge transfer

from the ligands to the metal ion and a delocalisation of the d electrons[40,51]. This being so, the magnetic data provide independent confirmation of the spectral evidence for greater covalency in the metal-sulphur bond.

For the CoL_2X_2 compounds the situation is complicated by the presence of low symmetry components of the ligand field produced by fundamentally different ligands in the coordination sphere. The differing Δ values of the CoL_2X_2 pairs, if operating independently of other effects, would reduce the difference in the magnetic moments by at least 0.1 B.M. Although the arsine sulphide halide complexes have magnetic moments 0.11 - 0.12 B.M. lower than their oxo-analogues, the differences between the corresponding pairs of phosphine oxide and sulphide complexes are negligible.

Effects of the Penultimate Ligand Atom

The present results provide information on the effects of phosphorus and arsenic on the bonding of the oxo- and thio-ligands. In the perchlorate complexes both trimethylphosphine oxide and sulphide produce lower ligand field splitting energies than

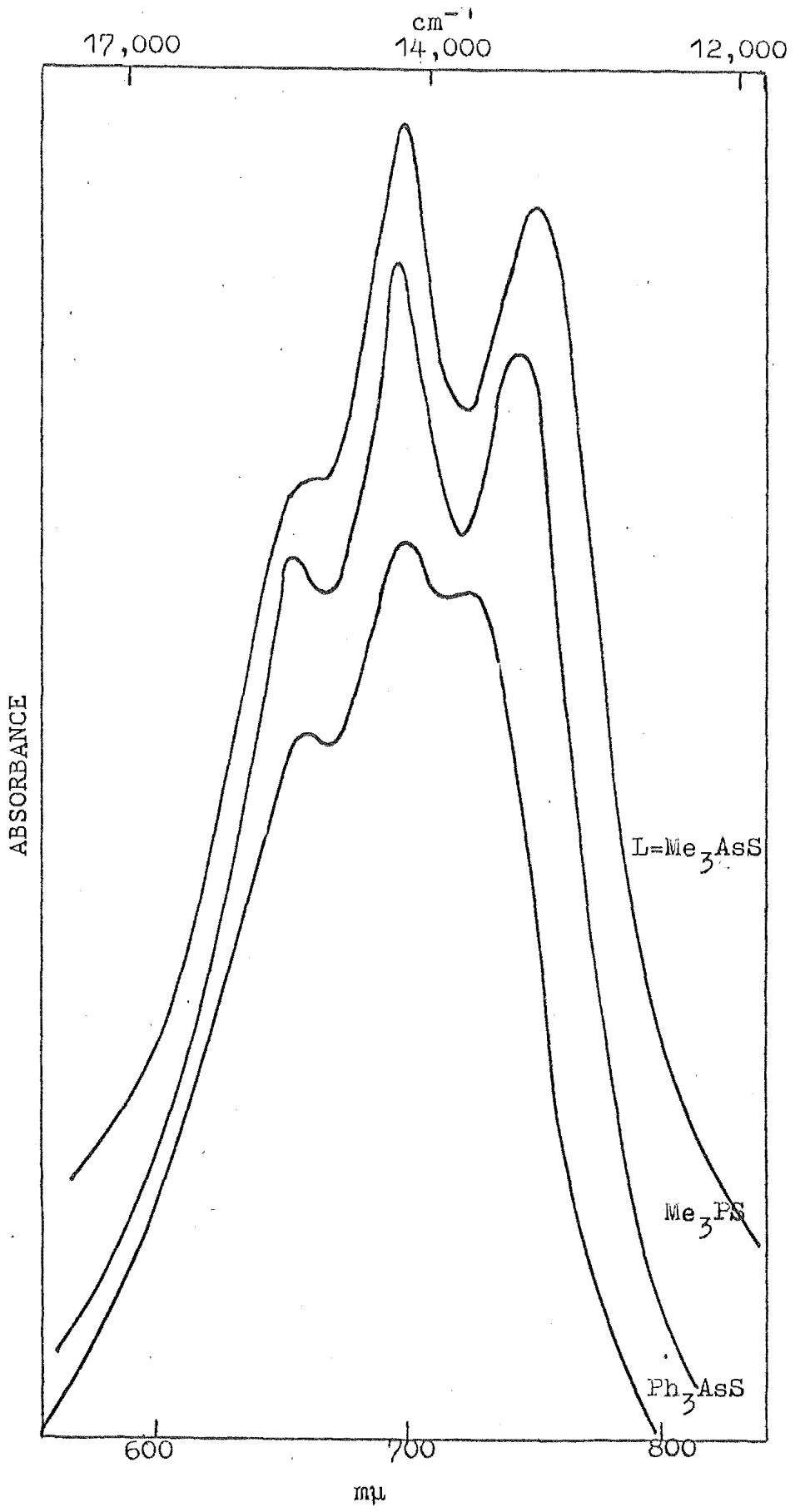


FIGURE 2a. ν_3 band profiles for solution spectra of $[CoL_4]^{2+}$ species.

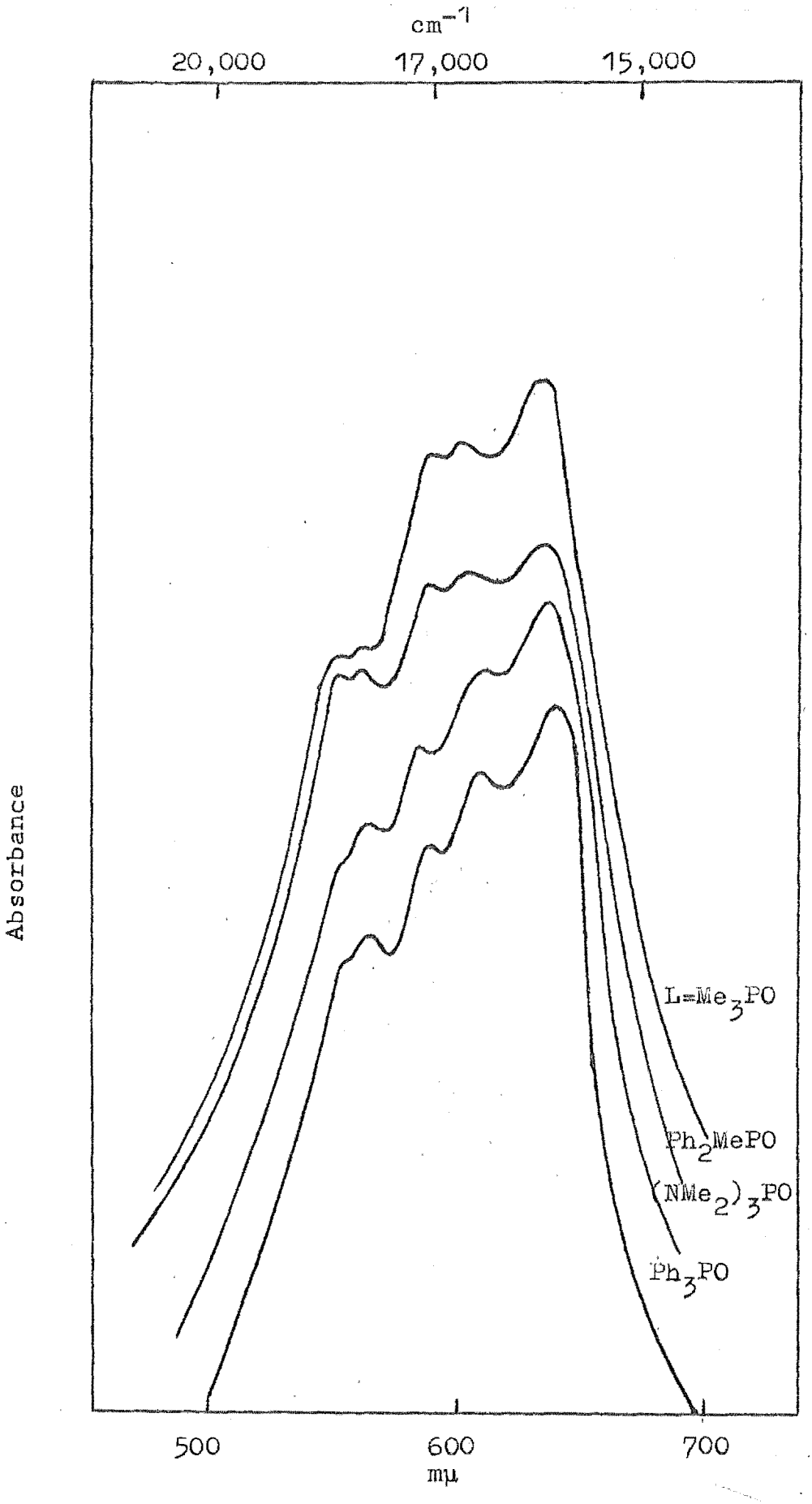


FIGURE 2b. $[CoL_4]^{2+}$ species (ref. 37b)

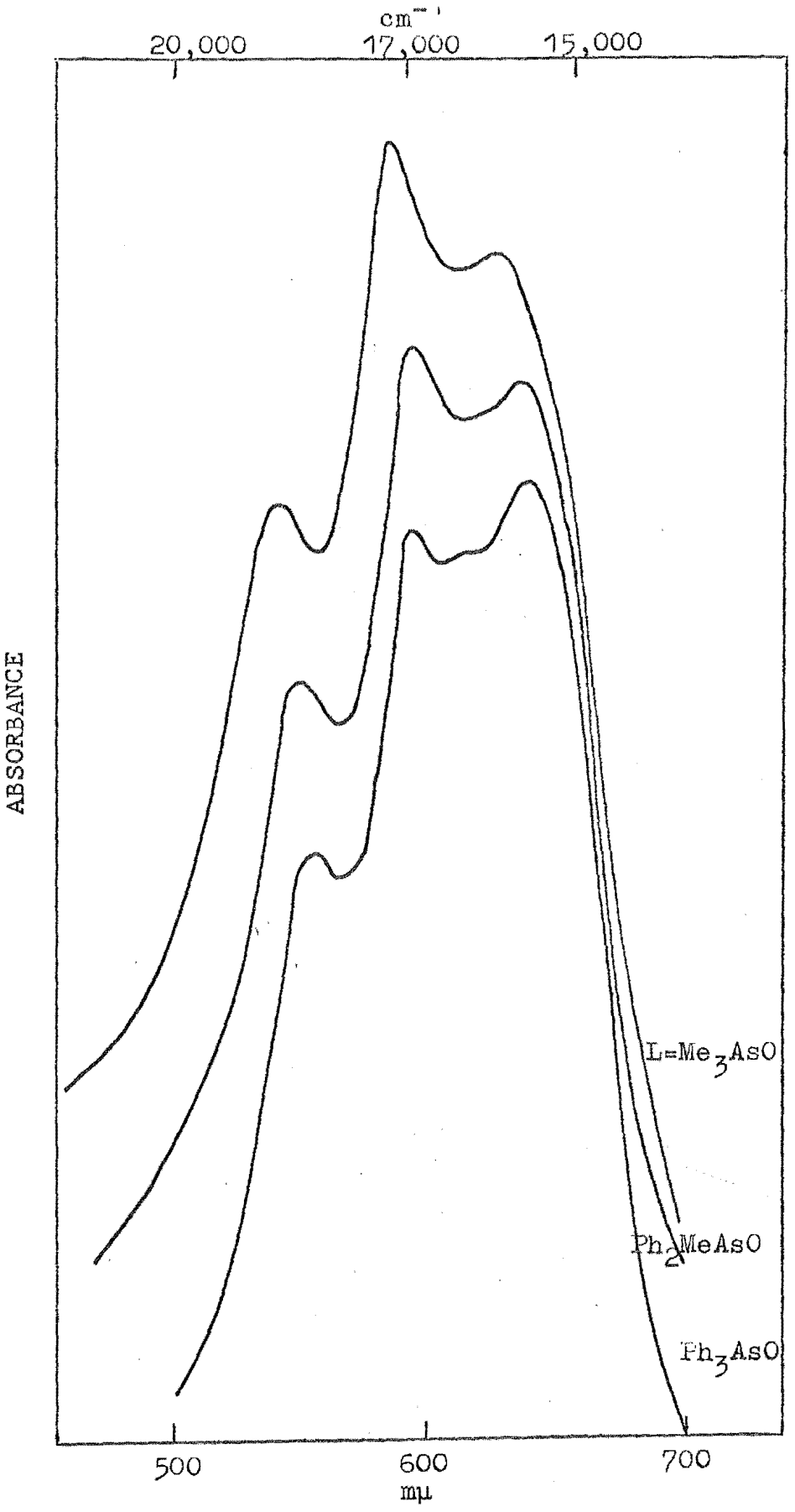


FIGURE 2c. $[CoL_4]^{2+}$ species (ref.37b)

their arsenic analogues (Table 4). There is evidence (see p.37) that the degree of d_π- p_π bonding in the P-O linkage in phosphine oxides is greater than in corresponding As-O linkages. This would lead to weaker donor properties and hence lower Δ values for phosphine oxides relative to arsine oxides. For the thio-ligands the situation is less certain (see p.37). However, while too much emphasis should not be placed on small differences in Δ, the values are always consistently lower for the $Co(Me_3PS)_2X_2$ complexes as compared with their Me_3AsS analogues, thus paralleling the situation for the $[CoL_4]^{2+}$ species.

$^4A_2 \rightarrow {}^4T_1(P)$ Transition

A further indication of the influence of the penultimate atom on the bonding of these ligands may be obtained from the details of the $^4A_2 \rightarrow {}^4T_1(P)$, ν_3 band profiles. In the free cobalt(II) ion there is a ^2G state close to the ^4P state and in the tetrahedral field the components of the former also lie close to the latter (Figure 1). It is considered that mixing of the $^4T_1(P)$ state and components of the ^2G state, through the action of spin orbit coupling leads to the structure of the ν_3 band[52,53].

For the thio-complexes, $[CoL_4](ClO_4)_2$ the profiles of the ν_3 band do not appear to be affected by the nature of the penultimate atom, (i.e. P or As). The band shapes and intensity distributions are virtually identical for the Me_3PS and Me_3AsS complexes and the spectrum of the Ph_3AsS complex is similar (Figure 2). In contrast the ν_3 band profiles for $[Co(Me_3PO)_4](ClO_4)_2$ and the isostructural $[Co(Me_3AsO)_4](ClO_4)_2$ are quite different from each other (Figure 2). This difference appears to be a function of the penultimate atom and not of Δ, because other oxo-ligands which produce different Δ values show a similar pattern[21,37b]. Thus complexes of Ph_3PO Ph_2MePO and $(Me_2N)_3PO$ have band profiles similar to that observed for Me_3PO, while the profiles for the complexes of the arsine oxides, Ph_3AsO and Ph_2MeAsO, compare closely to that of Me_3AsO (Figure 2). Differences in the $d_\pi - p_\pi$ bonding in the P-O and As-O bonds (see p.37) would lead to basic differences in the Co-O bond for the phosphine oxide and arsine oxide ligands, thus causing differences in the relative energies of the components of the ^2G and $^4T_1(P)$ states. This would lead to different spin-orbit coupling and consequently different band profiles. The fact that

the phosphine and arsine sulphides do not produce marked differences in the splitting of the ν_3 band would suggest that Co-S interactions are not affected by the penultimate atom (i.e. P or As) as appears the case for Co-O bonding.

$^4A_2 \rightarrow {}^4T_1(F)$ Transition

The action of spin orbit coupling would be expected to split the $^4A_2 \rightarrow {}^4T_1(F)$, ν_2 absorption band by no more than 1000 cm^{-1} (Figure 1). However, generally the observed splitting is greater than this and must be due to non-cubic elements of the ligand field, since there are no doublet levels close to the $^4T_1(F)$ state with which it could interact under the action of spin-orbit coupling[52,53]. The ν_2 bond also differs for the thio- and oxo-complexes $[CoL_4]^{2+}$. In the former case two main components occur while in the latter[21,37b] three bands are found. Unlike the ν_3 band, there is no apparent difference in the profiles for the phosphine and arsine oxide complexes. This is further evidence that the different profiles of the ν_3 bands can be related to different interactions between the components of the ^2G and ^4P states, since a reduction in symmetry will affect the ν_2 band

to a greater extent[52]. The observation of only two components in the γ_2 band may indicate that the thio-complexes are less distorted than the corresponding oxo-complexes, as might be expected for the larger sulphur atoms.

Infrared spectra

The assignment of infrared frequencies is facilitated by the simplicity of the spectra of the free ligands. For trimethylphosphine and arsine sulphides agreement between the observed frequencies and those given in the literature is generally satisfactory[54-56]. However, the As-O stretching frequency for trimethylarsine oxide in the present work was found to be at 870 cm^{-1} in contrast to a frequency of 903 cm^{-1} reported by Merijanian and Zingaro[18]. In this work the Me_3AsO spectrum, which was reproducible for different preparations and which confirmed the absence of water, was free of absorptions in the 900 cm^{-1} region. The remaining bands in the trimethylarsine oxide spectrum were assigned by comparison with the spectra of the related ligands, Me_3PO[57] and Me_3AsS[56] (see Table 7).

In the present work, the infrared spectra of the

$[ML_4](ClO_4)_2$ and ML_2X_2 complexes (where M = Co, Zn and L = Me_3AsS; M = Co and L = Me_3PS; M = Zn and L = Me_3AsO) have been assigned (Table 8). The spectra of the remaining tetrahedral oxo-complexes are reported in detail elsewhere[19,37]. Apart from a reduction in the As-O, P-S and As-S stretching frequencies, the main ligand bands are not significantly displaced upon coordination. The spectra of the $[CoL_4](ClO_4)_2$ complexes show single bands at about 1100 and 624 cm^{-1}, consistent with the presence of the uncoordinated perchlorate anion[59].

Metal-Halogen Stretching Frequencies The metal halogen stretching modes, ν(M-X), were identified as bands which show the usual decrease in frequency as the mass of the halogen is increased (Table 8). The frequencies of the M-X absorptions are in accord with the pseudo-tetrahedral structure assigned to the ML_2X_2 complexes[2,3].

Metal-Ligand Stretching Frequencies The metal-ligand stretching vibrations for the Me_3AsO complexes of zinc can be assigned to the new bands which appear between 450 and 400 cm^{-1} (Table 8). ν(M-O) bands are

found in the same general region for complexes of the related ligands Me_3PO and Ph_3AsO[9,19]. For the thio-ligand complexes the metal-ligand modes occur at 0.65 - 0.75 of the frequency of the corresponding ν(M-O) vibrations. Since the metal-halogen and metal-sulphur bands occur at similar frequencies in the chlorides, the only meaningful assignment is ν(M-Cl) + ν(M-S).

In the absence of definite evidence for stronger M-S(P) than M-S(As) bonding, it is reasonable to assume that the consistently lower ν(M-S) frequencies for the Me_3AsS complexes as compared with the Me_3PS complexes can be related to the greater mass of the arsenic atom. This implies that ν(P-S) and ν(As-S) are not pure stretching modes but contain some component involving movement of the phosphorus or arsenic atoms. Corresponding Me_3PO and Me_3AsO complexes show similar effects[21,37]. Both the solution and solid state spectra of the $[CoL_4](ClO_4)_2$ complexes show two ν(M-S) bands. For regular tetrahedral ML_4 complexes only one ν(M-S) would be predicted[60], but allowing for a probable reduction from 180° of the M-S-P (or M-S-As) bond angles, the highest possible symmetry is D_{2d}. On this basis at least two infrared

TABLE 7

Infrared Spectra (1200 - 400 cm^{-1}) of the Ligands[a]

Me_3PO[c]	Me_3PS[d]	Me_3AsO[b]	Me_3AsS[d]	Assignment
1166s				ν(P-O)
960s	979s	926s	930s	CH_3 def.
944s	948s	913sh		
		870s		ν(As-O)
870m	865m	848m	847m	CH_3 def.
863m		836m		
741m	745m			ν_{as}(P-C)
e	713m			ν_s(P-C)
		638m[f]	628m	ν_{as}(As-C)
		625m		
		g	594m	ν_s(As-C)
	565s			ν(P-S)
			476s	ν(As-S)

[a] As nujol mulls

[b] Me_3AsO spectrum assigned in present work.

[c] Complete assignment for Me_3PO reported in refs. 54,57,58.

[d] Partial assignments for Me_3PS and Me_3AsS reported in refs. 56,55.

[e] ν_s(P-C) not observed

[f] ν_{as}(As-C) is not generally split in complexes.

[g] ν_s(As-C) not observed.

TABLE 8a

Infrared Spectra (cm^{-1}) of Co and Zn tetrahedral complexes[a]

Compound	ν(P-O), ν(As-O) ν(P-S)	ν(M-O), ν(M-S)	ν(M-X)	Other Bands (500-200cm^{-1})
Me_3PO	-	-	-	375sh, 365m, 315w, 242vw
$[Co(Me_3PO)_4](ClO_4)_2$[b]	c	460sh, 448m	-	352m, 328w, 255vw
Me_3AsO	870s	-	-	266m
$[Co(Me_3AsO)_4](ClO_4)_2$[b]	862sh, 837s	442sh, 428s	-	271m, 263sh
$[Zn(Me_3AsO)_4](ClO_4)_2$	870s, 841s	430s, br	-	273m, 266sh
$Zn(Me_3AsO)_2Cl_2$	880sh, 863s, 842sh	413s, br	289sh, 280s	261m
$Zn(Me_3AsO)_2Br_2$	897sh, 862s, 841sh	411s, br	213s, br	276m, 260m
Me_3PS	565s	-	-	280vw, 225vw
$[Co(Me_3PS)_4](ClO_4)_2$	538sh, 530s, 525sh	330m, 321m 330m, 323sh[d]	-	290vw, 260vw, 225vw
$Co(Me_3PS)_2Cl_2$	538sh, 533s	(325sh, 320s, 308s, 282m)[e]		255vw
$Co(Me_3PS)_2Br_2$	536s	316m, 310m	246sh, 240s	275vw, 258w
$Co(Me_3PS)_2I_2$	531s	317m, 311m	-	275vw, 257w

[a] For Nujol mulls

[b] From refs. 21,37; for $Co(Me_3PO)_2X_2$ and $Co(Me_3AsO)_2X_2$ complexes see refs 19,21,37.

[c] Obscured by perchlorate absorption

[d] Values for nitromethane solution

[e] ν(M-S) + ν(M-Cl).

TABLE 8b

Infrared Spectra (cm^{-1}) of Co and Zn tetrahedral complexes[a]

Compound	ν(As-S)	ν(M-S)	ν(M-X)	Other Bands (500 - 200cm^{-1})
Me_3AsS	476s	-	-	-
$[Co(Me_3AsS)_4](ClO_4)_2$	442s, 437sh	312m, 294mw 312m, 295m[b]	-	-
$Co(Me_3AsS)_2Cl_2$	442s	(315s, 308s, 303s, 288s)[c]		-
$Co(Me_3AsS)_2Br_2$	440s	299m, 288m	238s, 224m	-
$Co(Me_3AsS)_2I_2$	440s	298m, 285m	-	-
$Co(Me_3AsS)_2(NCS)_2$	444s	291m	327m	-
$[Zn(Me_3AsS)_4](ClO_4)_2$	444s	287m 289m, 277sh[b]	-	-
$Zn(Me_3AsS)_2Cl_2$	446s	(294s, 288s, 280s, 276s)[c]		-
$Zn(Me_3AsS)_2Br_2$	452s, 446s	282m, 277sh	214s, br	-
Ph_3AsS	495s	-	-	474m, 467m, 457w, 345m, 326m, 297vw
$[Co(Ph_3AsS)_4](ClO_4)_2$	d	282m, 275m	-	475m, 464s, 455sh, 441sh, 345s, 330sh, 297vw
$Co(Ph_3AsS)_2Br_2$	d	(260sh, 250m, 245m)[e]		469s, 444m, 348s, 343s, 298vw
$[Zn(Ph_3AsS)_4](ClO_4)_2$	d	275m	-	477m, 465s, 455sh, 446sh, 346s, 337sh.

[a] For Nujol mulls [b] Values for nitromethane solution [c] ν(M-S) + ν(M-Cl)

[d] For the complexes ν(As-S) is indistinguishable from other ligand bands

[e] ν(M-S) + ν(M-Br).

active M-S stretching frequencies should be observed[61]. In all cases the ν(M-O), ν(M-S) and ν(M-X) values for the zinc complexes are lower than those of the corresponding cobalt complexes, as has been noted for other cobalt-zinc systems[61,62].

$Co(Me_3AsS)_2(NCS)_2$ The infrared spectrum with ν(C-N) at 2085, 2065 cm^{-1} and ν(C-S) at 840 cm^{-1} shows that the complex contains nitrogen bonded thiocyanate. The ν(C-S) frequency is above the ranges corresponding to sulphur bonded (690 - 720 cm^{-1}) or bridged thiocyanate (740 - 780 cm^{-1}) systems[63,64]. The ν(Co-N) and ν(Co-S) bands lie at 327 and 291 cm^{-1}. The latter is tentatively assigned as ν(Co-S) since it falls in the range 312 - 285 cm^{-1} found for this mode in other tetrahedral trimethylarsine sulphide complexes of cobalt(II).

Triphenylarsine Sulphide Complexes The As-S stretching vibration for uncomplexed triphenylarsine sulphide is found at a frequency of 495 cm^{-1}, somewhat above strong ligand absorptions at 475 - 450 cm^{-1}. In the complexes, the ν(As-S) band was indistinguishable from the other ligand bands indicating a decrease of

over 20 cm^{-1} in the frequency upon coordination. Assignment of the metal-ligand modes is complicated by ligand absorptions occurring between 350 and 290 cm^{-1}. The medium bands in the 282 - 270 cm^{-1} range are assigned to metal-ligand stretching vibrations (Table 8). The $\nu(M-S)/\nu(M-O)$ ratio for the $[CoL_4](ClO_4)_2$ complexes (L = Ph_3AsS and Ph_3AsO) is 0.68, within the range (0.65 - 0.75) found for the trimethyl derivatives. For the $Co(Ph_3AsS)_2Br_2$ complex the $\nu(M-S)$ and $\nu(M-Br)$ modes occur at similar frequencies preventing separate assignment.

The Nature of the P-S and As-S Bonds

There is considerable evidence that π bonding in the P-O linkage in phosphine oxides is important[65-68]. The bond may be regarded as a coordinate bond ($P \rightarrow O$ bond) on which is superimposed a $d_\pi - p_\pi$ component, arising from donation of electrons from the filled p_π orbitals of the oxygen into the empty d_π orbitals of the phosphorus[69]. It appears that there is weaker π bonding in the As-O bond of arsine oxides[37b,67]. Less is known about the P-S and As-S bonds in the corresponding sulphides.

The main evidence for π bonding in the sulphides

(R_3PS and R_3AsS) comes from the P-S and As-S stretching frequencies. Electronegative R substituents attached to the penultimate atom would be expected to increase the stability of a π bond, whereas if the bond was a simple coordinate bond, the reverse would be anticipated. From Table 10 it is seen that ν(P-S) frequencies are increased by the more electron withdrawing R groups, and that ν(As-S) frequencies are also influenced by substituent groups. However arsine sulphides containing highly electronegative groups (Cl_3AsS for example) have not been synthesised. Phosphine oxides are included in Table 10 for comparison.

While a number of factors influence the position of the ν(P-O) absorption in complexes, the lowering of the frequency upon coordination can be related mainly to a reduction of the $d_\pi - p_\pi$ component in the P-O linkage[69]. That a similar decrease in the ν(P-S) and ν(As-S) frequencies (Table 9) is observed is further evidence for π bonding in the P-S and As-S bonds.

The available evidence indicates that although π bonding is important in the P-S and As-S bonds, it is less extensive than in corresponding P-O bonds[68]. The dissociation energies of P-S bonds ($\sim$ 95 kcal./mole) are some 35 - 65 kcal./mole lower than of P-O bonds

(125 - 155 kcal/mole)[65]. Moreover, it appears that the increase in strength on passing from a single P-O bond to a P=O bond in an R_3PO compound is greater than that on passing from a single P-S bond to a P=S bond in a corresponding phosphine sulphide. The difference between P-O and P=O (in R_3PO) is about 55 kcal/mole compared with 26 kcal./mole between P-S and P=S (in R_3PS)[70]. P^{31} chemical shifts (δ) are always lower for phosphine sulphides. The δ values for Me_3PO (- 36ppm) and Me_3PS (- 59ppm) indicate lower nuclear shielding of the phosphorus atom in the sulphide due to a lower d_π orbital occupancy[71].

Little is known about the relative degree of bonding in the P-S and As-S bonds although Me_3AsS produces greater Δ values than Me_3PS in corresponding cobalt(II) complexes (Table 4), probably indicating the Me_3AsS ligand has stronger bonding properties and therefore a weaker As-S π component.

TABLE 9

Shifts in P-O, P-S, As-O and As-S Stretching Frequencies on coordination [a]

Compound	Shift(cm^{-1})	Compound	Shift(cm^{-1})
$[Co(Me_3PS)_4](ClO_4)_2$	-34	$[Co(Me_3PO)_4](ClO_4)_2$	b
$Co(Me_3PS)_2Cl_2$	-29	$Co(Me_3PO)_2Cl_2$	-56
$Co(Me_3PS)_2Br_2$	-29	$Co(Me_3PO)_2Br_2$	-56
$Co(Me_3PS)_2I_2$	-34	$Co(Me_3PO)_2I_2$	-45
$[Co(Me_3AsS)_4](ClO_4)_2$	-36	$[Co(Me_3AsO)_4](ClO_4)_2$	-25
$Co(Me_3AsS)_2Cl_2$	-34	$Co(Me_3AsO)_2Cl_2$	-23
$Co(Me_3AsS)_2Br_2$	-36	$Co(Me_3AsO)_2Br_2$	-26

[a] Thio-complexes this work; oxo-complexes from refs. 19,21,37; for split bands average value of shift has been taken.

[b] ν(P-O) obscured by ClO_4^- absorption.

TABLE 10

P-O, P-S and As-S Stretching Frequencies (cm^{-1})

R_3PO	Cl_3PO	Ph_3PO	Me_3PO	P-O(Calc) [a]
ν(P-O)	1290 [b]	1195 [b]	1166	765
R_3PS	Cl_3PS	Ph_3PS	Me_3PS	P-S(calc)
ν(P-S)	750 [b]	637	565	480
R_3AsS		Ph_3AsS	Me_3AsS	As-S(calc)
ν(As-S)		495	476	370

[a] Estimated frequency for single bond, using equation of Gordy (ref. 56,10).

[b] Ref. 10 and refs. therein.

CHAPTER 2

BRIDGED OCTAHEDRAL TRIMETHYLARSINE OXIDE COMPLEXES OF Fe(II), Co(II) AND Ni(II) AND TETRAHEDRAL TRIMETHYLARSINE SULPHIDE COMPLEXES OF Fe(II) AND Ni(II)

INTRODUCTION

Both trimethylarsine oxide and sulphide react with cobalt(II) to give structurally analagous pairs of complexes (Chapter 1). A wider study shows that corresponding pairs of oxo- and thio-complexes of iron(II) and of nickel(II), although stoichiometrically the same, have different structures (Table 11). Thus the trimethylarsine oxide perchlorate complexes $[ML_4(ClO_4)]ClO_4$ (where M = Fe and Ni) are five-coordinate, whereas the corresponding thio-complexes contain the tetrahedral $[ML_4]^{2+}$ cation. With the halides, trimethylarsine sulphide continues to give tetrahedral ML_2X_2 complexes but trimethylarsine oxide appears to act as a bridging group, giving rise to octahedral polymers. Evidence on the mode of bridging is obtained from the infrared spectra of the analogous $ML_2(NCS)_2$ thiocyanate complexes. Cobalt halides also react with trimethylarsine oxide to give bridged octahedral complexes, as well as the tetrahedral isomers described previously (Chapter 1).

This chapter is concerned primarily with the bridged octahedral trimethylarsine oxide complexes and the tetrahedral trimethylarsine sulphide complexes. The five-coordinate trimethylarsine oxide perchlorate complexes are discussed in Chapter 3.

TABLE 11

Me_3AsO and Me_3AsS Complexes of the First Row Divalent Transition Metals

Complex	Structure[a]	L	M
$[ML_4](ClO_4)_2$	tetr.	Me_3AsO	Co,Zn
		Me_3AsS	Fe,Co,Ni,Zn
$[ML_4(ClO_4)]ClO_4$	5-coord.	Me_3AsO	Mn,Fe,Ni,Cu
$[ML_5](ClO_4)_2$	5-coord.	Me_3AsO	Mn,Co,Ni
ML_2X_2 (X= Cl,Br)	tetr.	Me_3AsO	Co,Zn
		Me_3AsS	Fe,Co,Ni,Zn
ML_2X_2 (X = Cl,Br)	bri. oct.	Me_3AsO	Fe,Co,Ni

[a] tetr. = tetrahedral, bri. oct. = bridged octahedral

RESULTS AND DISCUSSION

Trimethylarsine Oxide Complexes

Trimethylarsine oxide reacts readily with the divalent salts of iron and nickel. Complexes of the type $M(Me_3AsO)_2X_2$ are formed with the chlorides and bromides of iron and nickel. The iron(II) compounds, which are rapidly oxidised, were prepared and stored under nitrogen. Depending on the reaction conditions two distinct products can be isolated from the reaction of trimethylarsine oxide with cobalt(II) chloride. An intense blue tetrahedral complex $Co(Me_3AsO)_2Cl_2$ (Chapter 1) is obtained from cold acetone solutions, while reaction in hot ethanol gives a pale blue compound with the same formula. Similarly two products are obtained with cobalt(II) bromide although the pale blue isomer is more difficult to isolate, (p.103) and electronic reflectance spectra indicate that it still contains some of the tetrahedral form. The pale blue bromide complex $Co(Me_3AsO)_2Br_2$ reverts completely to the tetrahedral isomer upon dissolving in nitromethane, heating to 100° or on exposure to atmospheric moisture.

X-ray powder photographs show the compounds

$Fe(Me_3AsO)_2X_2$, $Co(Me_3AsO)_2X_2$ (pale blue forms) and $Ni(Me_3AsO)_2X_2$ (where X = Cl and Br) to be isomorphous.

Electronic Spectra

The insolubility of the isomorphous $M(Me_3AsO)_2X_2$ complexes prevents the measurement of their solution spectra. Reflectance spectra (Table 12) however, are typical of high spin octahedral iron(II), cobalt(II) and nickel(II) compounds[72,73]. The spectrum of octahedral $Co(Me_3AsO)_2Br_2$ indicates that it still contains some tetrahedral impurity.

The spectra of the $Fe(Me_3AsO)_2X_2$ compounds show one assymmetric band (Figure 3) consisting of a maximum at about 8000 cm^{-1} and a shoulder at about 6000 cm^{-1}, which can be assigned to the $^5T_{2g} \rightarrow {}^5E_g$ transition[72]. A splitting of the ^5E_g state under the influence of the ligand field will cause the observed doublet structure of the absorption[74].

The spectra of the cobalt complexes are more difficult to interpret. For octahedral cobalt(II) three bands corresponding to the spin allowed transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ (ν_2), and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) are expected[72]. The transition $^4T_{1g}(F) \longrightarrow {}^4A_{2g}$ corresponds to a two

electron jump and is therefore weak and often obscured[72]. The spectrum of octahedral $Co(Me_3AsO)_2Cl_2$ shows two strong bands at 5,700 cm^{-1} and 17,000 cm^{-1}, and a weak band at 11,200 cm^{-1} (Table 12 and Figure 4). The low energy band has been assigned to the ν_1 transition and the high energy band to the ν_3 transition [75,76]. The ν_3 band is structured, probably due to distortions of the ligand field and the presence of spin-forbidden transitions which gain intensity by mixing with the spin allowed transition[75,76]. The assignment of the weak band at 11,200 cm^{-1} to the ν_2 transition seems reasonable since the energy of this transition should be approximately twice that of the ν_1 transition[76].

For octahedral nickel(II) complexes three absorption bands corresponding to the spin-allowed transitions $^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1), $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3) should be observed. Spin-forbidden triplet to singlet transitions may also appear[72]. The spectra of the $Ni(Me_3AsO)_2X_2$ complexes (Table 12) have three main bands (Figure 5). The lowest energy band is assigned to the ν_1 and the 11,000 - 13,000 cm^{-1} band to the ν_2 transitions respectively. The splitting of the ν_2 band and the broadness of ν_1 probably indicate

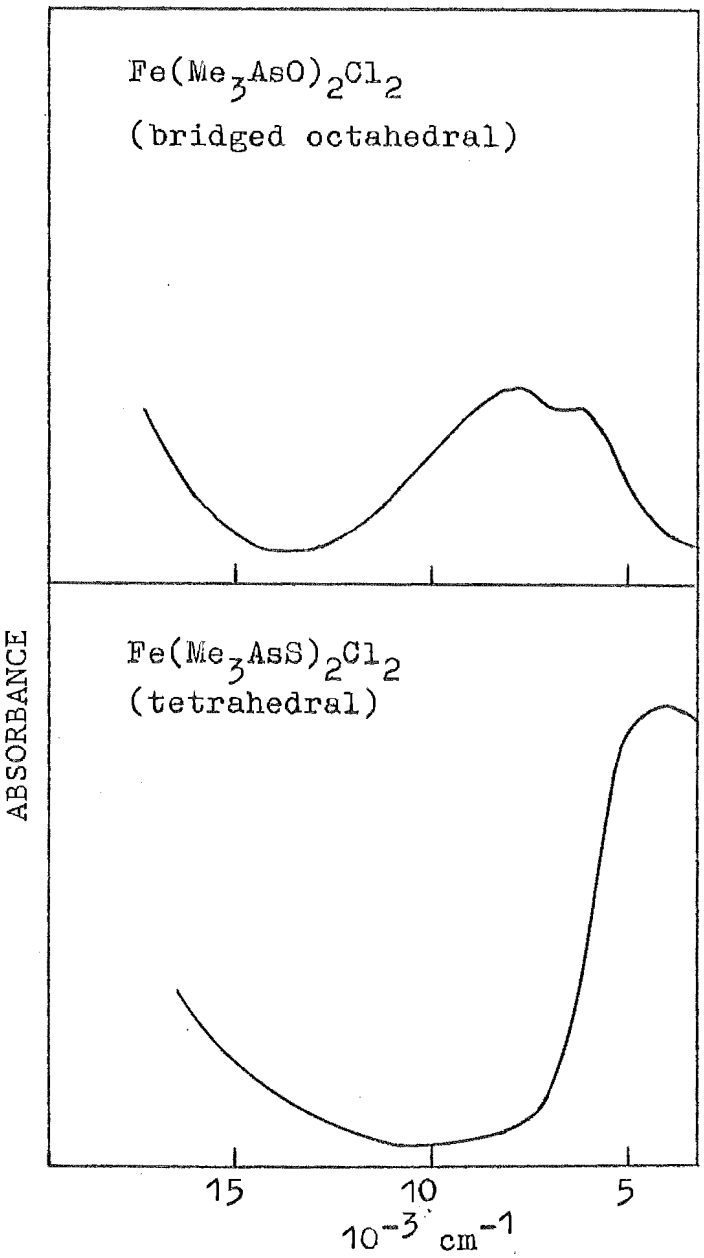


FIGURE 3. Electronic spectra of Iron(II) complexes. (reflectance)

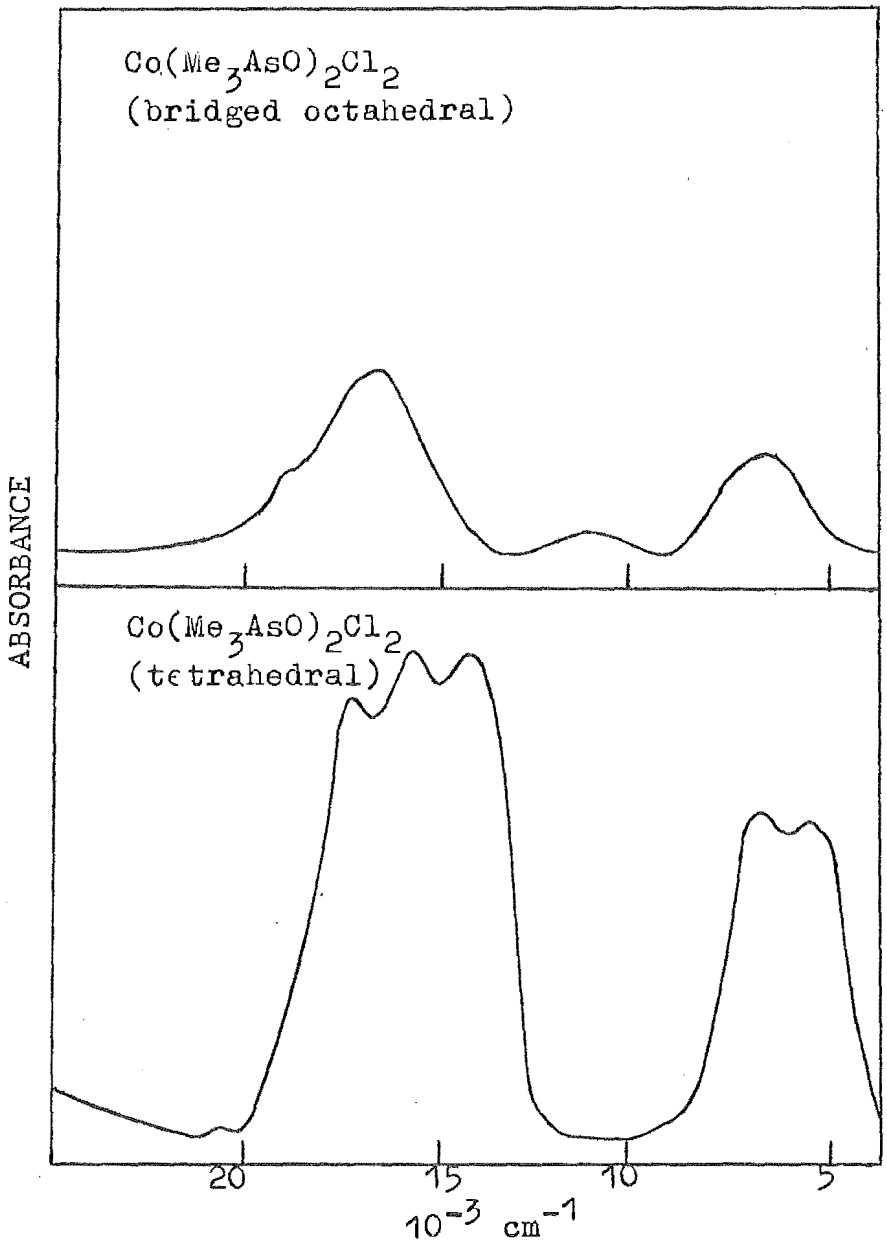


FIGURE 4. Electronic spectra of Cobalt(II) complexes. (reflectance)

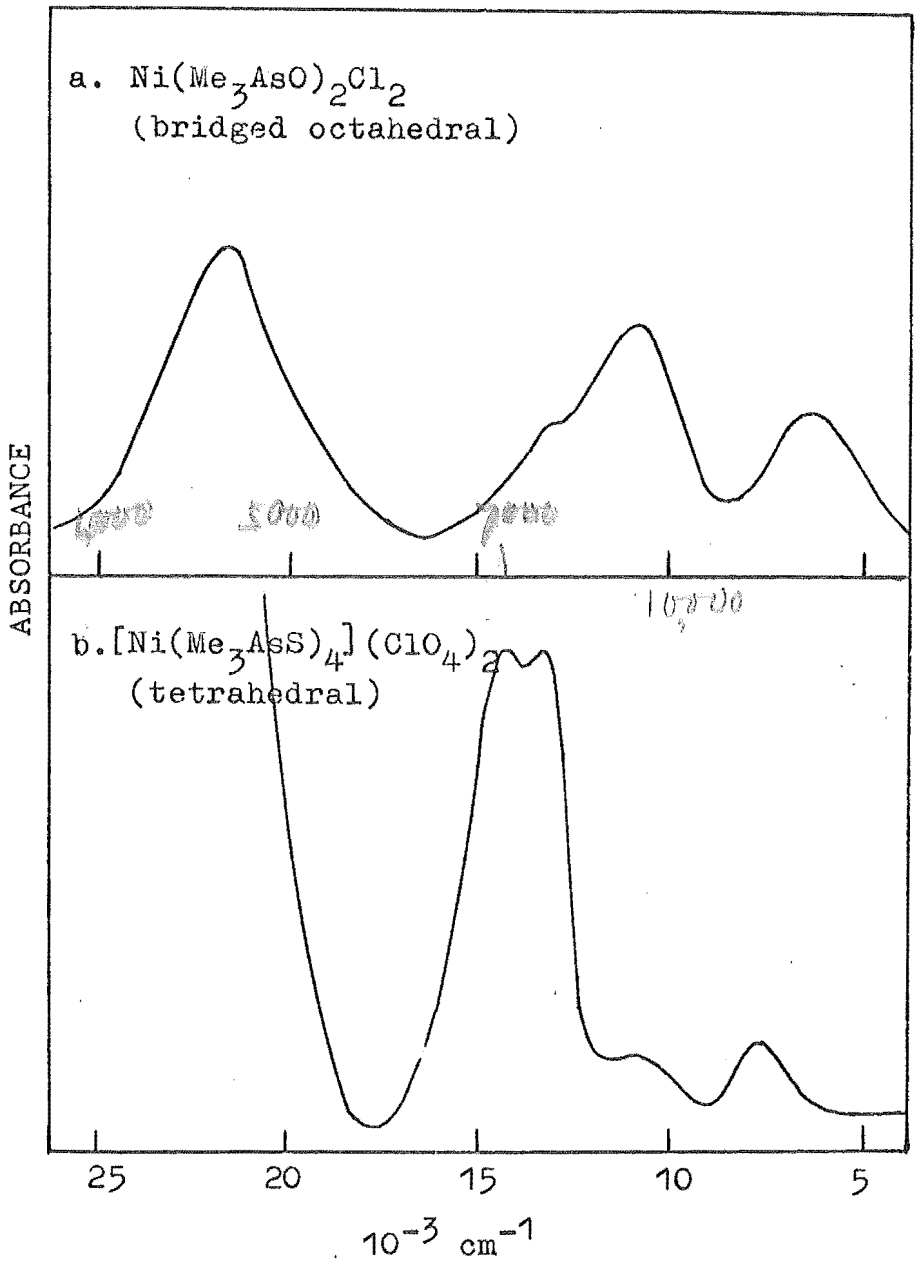


FIGURE 5. Electronic spectra of Nickel(II) complexes. (a. reflectance, b. nitromethane solution)

TABLE 12

Reflectance Spectra of Bridged Octahedral Complexes

$Fe(Me_3AsO)_2Cl_2$	8,000m, 6,100sh
$Fe(Me_3AsO)_2Br_2$	7,900m, 6,100sh
$Co(Me_3AsO)_2Cl_2$ [a]	18,600sh, 17,000m, 11,200w, 5,700m br
$Co(Me_3AsO)_2(NCS)_2$ [b]	19,900sh, 18,200m, 14,400 w sh, 7,600 m br
$Ni(Me_3AsO)_2Cl_2$	21,700m, 13,000sh, 11,100m, 6,500 w br
$Ni(Me_3AsO)_2Br_2$	21,300m, 12,500sh, 10,900m, 6,400w br
$Ni(Me_3AsO)_2(NCS)_2$	23,700m, 13,900sh, 13,100m, 7,900m br
$Ni(Me_3PO)_2(NCS)_2$	23,800m, 14,000sh, 13,000m, 8,000m br

[a] Bromide contains tetrahedral impurities

[b] From refs. 21,37.

TABLE 13

Electronic Spectral Parameters for Bridged Octahedral Complexes

Compound	$\Delta(cm^{-1})$	$B'(cm^{-1})$	β^a
$Fe(Me_3AsO)_2Cl_2$	7,000	-	-
$Fe(Me_3AsO)_2Br_2$	7,000	-	-
$Co(Me_3AsO)_2Cl_2$	6,600	870	0.90
$Co(Me_3AsO)_2(NCS)_2$	8,700	840	0.86
$Ni(Me_3AsO)_2)Cl_2$	6,500	950	0.90
$Ni(Me_3AsO)_2Br_2$	6,400	920	0.87
$Ni(Me_3AsO)_2(NCS)_2$	7,900	900	0.85
$Ni(Me_3PO)_2(NCS)_2$	8,000	890	0.84

[a] $\beta = B'/967$ and $B'/1056$ for Co(II) and Ni(II) complexes respectively.

TABLE 14

Magnetic Data for Bridged Octahedral Complexes

Compound	T (^{o}K)	χ_m(X10^3) (cgsu)	χ_m^{corr}(X10^3) (cgsu) [a]	μ (B.M.)
$Co(Me_3AsO)_2Cl_2$	293	11.47	11.70	5.26
$Ni(Me_3AsO)_2Cl_2$	296	4.32	4.54	3.29
$Ni(Me_3AsO)_2Br_2$	292	4.77	5.03	3.44

[a] Corrected for diamagnetism

distortions from octahedral symmetry, although the ν_2 absorption may also include the spin forbidden $^3A_{2g} \longrightarrow {}^1Eg$ transition[72,77]. The 21,000 - 22,000 cm^{-1} band is assigned to the ν_3 transition.

Electronic Spectral Parameters

Assuming regular octahedral symmetry for the complexes, the ligand field parameters Δ and β, can be calculated (Appendix II). For the iron(II) and nickel(II) complexes, the values of the $^5T_{2g} \longrightarrow {}^5Eg$ and $^3A_{2g} \longrightarrow {}^3T_{2g}$ transitions correspond to Δ. The parameters for the cobalt(II) complex have been calculated from the energies of the ν_1 and ν_3 bands, using the equations derived from the energy matrices of Tanabe and Sugano[39]. The values of Δ for the bridged octahedral complexes are at the low end of the range (6,000 - 13,000 cm^{-1}) generally observed for the divalent ions of the first row transition series in an octahedral field[78].

Magnetic Susceptibilities

The magnetic moments lie in the range normally observed for high spin octahedral complexes[73]. (Table 14). The instability of the $Fe(Me_3AsO)_2X_2$ and $Co(Me_3AsO)_2Br_2$ compounds prevents the measurement of

their magnetic moments. The magnetic moment of octahedral $Co(Me_3AsO)_2Cl_2$ is 5.26 B.M. which can be compared with the value of 4.26 B.M. observed for the tetrahedral isomer (Chapter 1). In an octahedral field cobalt(II) has an orbitally degenerate ground state ($^4T_{1g}$) which causes an orbital angular momentum contribution to the magnetic moment[73]. Nickel(II) in an octahedral field has a $^3A_{2g}$ ground state for which no orbital contribution to the magnetic moment is expected. However, since the ligand fields produced in the $Ni(Me_3AsO)_2X_2$ complexes are weak (Table 13) a mixing in of the $^3T_{1g}$ first excited state with the ground state under the action of spin-orbit coupling may have an appreciable effect[77]. Yet the values observed (3.3 - 3.4 B.M.), are still considerably lower than those found for the tetrahedral $Ni(Ph_3AsO)_2X_2$ complexes (3.9 - 4.0), which have an orbitally degenerate ground state[79].

Infrared Spectra (1,000 - 500 cm^{-1})

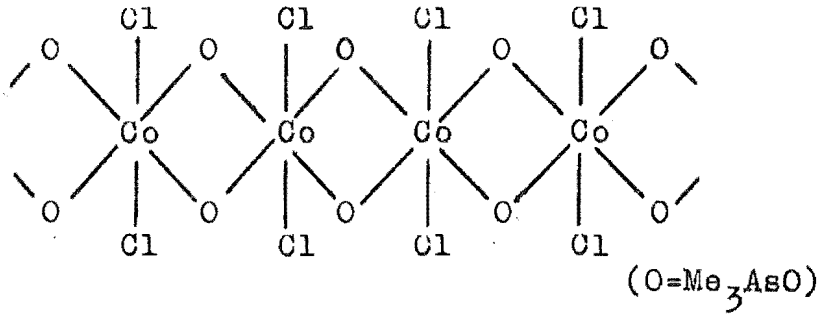
The electronic spectra and magnetic moments of the isomorphous series of $M(Me_3AsO)_2X_2$ (where M = Fe, Co and Ni; X = Cl and Br) complexes indicate that they must have essentially octahedral and therefore

polymeric structures. The insolubility of the complexes is consistent with their polymeric nature. Polymerisation may be achieved either through the halogen or the trimethylarsine oxide functioning as bridging groups. Polymers of the general formula ML_2X_2, for which halogen bridging has been established, are known with such ligands as water[80] and pyridine[81]. However in the present work, infrared evidence suggests that the $M(Me_3AsO)_2X_2$ complexes contain oxo- rather than halogen bridges (Figure 6).

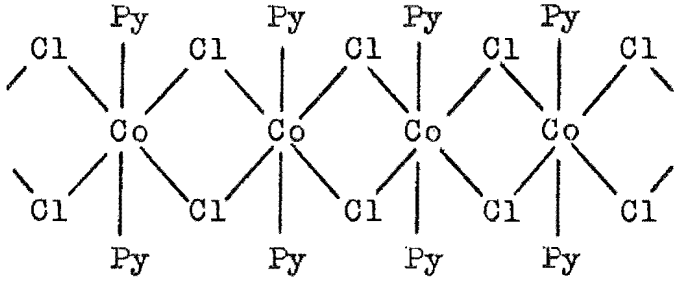
The As-O stretching frequency for uncoordinated trimethylarsine oxide is observed at 870 cm^{-1}. Complex formation lowers the frequency to 855 - 866 cm^{-1} in the five-coordinate complexes (Table 28) and to 830 - 870 cm^{-1} in the tetrahedral complexes (Table 8). In an octahedral complex containing unidentate Me_3AsO groups the average ν(As-O) frequency is raised on coordination to 880 and 866 cm^{-1} (Table 28). The average value of the ν(As-O) band in the spectra of the polymeric octahedral $M(Me_3AsO)_2X_2$ complexes is significantly lower (Table 15 and Figure 7). The absorption consists of two components, in the 830 - 860 and 765 - 800 cm^{-1} regions respectively. The difference in energy between the two components is

metal sensitive and increases on passing from iron ($\sim$40 cm^{-1}) to cobalt ($\sim$60 cm^{-1}) to nickel ($\sim$80 cm^{-1}). For the same metal, the ν(As-O) frequencies are consistently 10 - 20 cm^{-1} higher for the chlorides than for the bromides. A weak methyl deformation mode usually appears at 837 - 839 cm^{-1} but does not interfere with the assignment of ν(As-O).

The low average value of the ν(As-O) absorption suggests that the trimethylarsine oxide is acting as a bridging ligand. In complexes where triphenylarsine oxide[33], pyridine N-oxide[82] and thiourea[83] have been definitely established to act as bridging ligands, the respective ν(As-O), ν(N-O) and ν(C-S) absorptions occur at lower frequencies than for related complexes in which the ligands are unidentate. For example $HgCl_2(Ph_3AsO)_2$ and $[HgCl_2(Ph_3AsO)]_2$ both contain mercury in a distorted tetrahedral field of two oxygen and two chlorine atoms[84,33]. The ν(As-O) frequency for the latter compound[32], which contains Ph_3AsO bridges, is at 810 cm^{-1} compared with the value of 860 - 880 cm^{-1} found for $HgCl_2(Ph_3AsO)_2$ which contains unidentate arsine oxide groups. Lower ν(As-O) frequencies would perhaps be expected for bridging arsine oxide groups as a result of a greater electron



a. Proposed structure for bridged octahedral complexes, $M(Me_3AsO)_2X_2$ e.g. M = Co and X= Cl.



b. Structure of bridged octahedral $Co(py)_2Cl_2$.

FIGURE 6. Structures of bridged octahedral complexes.

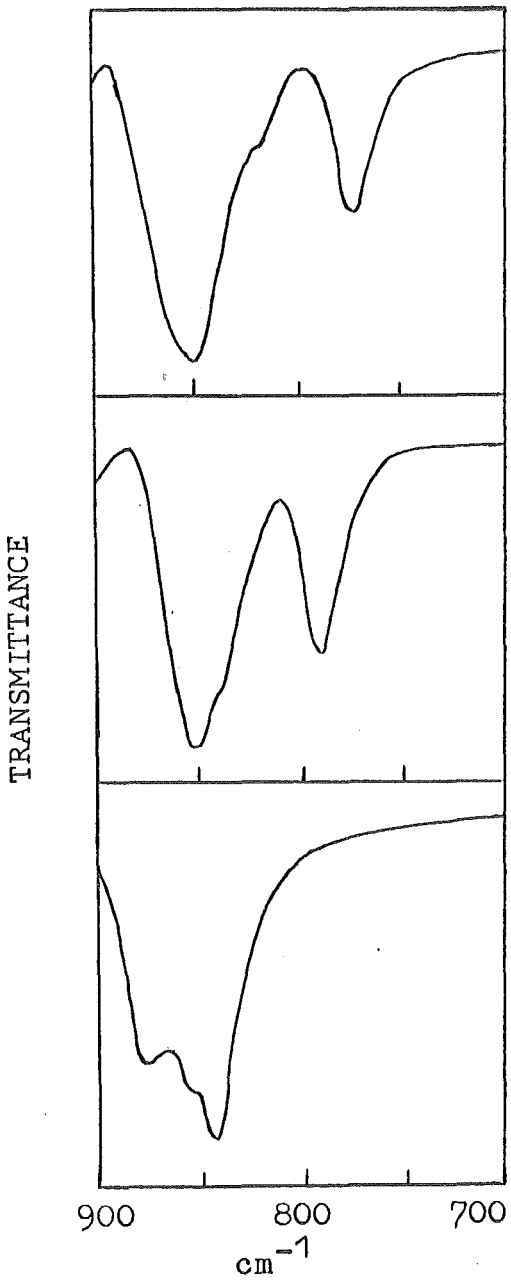


FIGURE 7. Infrared spectra in the As-O stretching region.

TABLE 15

Infrared Spectra of Bridged Octahedral Complexes (cm^{-1}) [a]

Compound	ν(As-O)	ν(M-O)	ν(M-X)	Other Bands (500 - 200 cm^{-1})
Me_3AsO	870s	-	-	266m
$Fe(Me_3AsO)_2Cl_2$	847s, 802m	395s, 360w sh	241m	289m
$Fe(Me_3AsO)_2Br_2$	830s, 787m	390s, 343w sh	-	286m
$Co(Me_3AsO)_2Cl_2$	850s, 789m	400s, 355w sh	240m	289m
$Co(Me_3AsO)_2Br_2$	833s, 775m	399s, 355w sh	-	273m
$Co(Me_3AsO)_2(NCS)_2$	841s, 771m	397s	-	280m br [b]
$Ni(Me_3AsO)_2Cl_2$	861s, 778m	415s	255m	293m
$Ni(Me_3AsO)_2Br_2$	846s, 765m	410s, 355w sh	-	291m
$Ni(Me_3AsO)_2(NCS)_2$	850s, 774m	425s, 390w sh	-	302m br [b]
Me_3PO	1166s [c]	-	-	375sh, 363m, 315m, 242w
$Ni(Me_3PO)_2(NCS)_2$	1137m, 1083s	445s, 409sh	259m	377m, 359m, 328w

[a] As Nujol mulls

[b] Includes ν(M-N)

[c] ν(P-O)

TABLE 16

Infrared Frequencies (cm^{-1}) of the thiocyanate group in related metal complexes

Complex	ν(C-N)	ν(C-S)	δ(NCS)	NCS Type[a]	Ref.
$Co(Me_3AsO)_2(NCS)_2$	2073	b	480	N	c
$Ni(Me_3AsO)_2(NCS)_2$	2090	b	481	N	c
$Ni(Me_3PO)_2(NCS)_2$	2090	807	480	N	c
$Co(tu)_2(NCS)_2$	2072	816	-	N	83
$Ni(tu)_2(NCS)_2$	2088	812	-	N	63
$Co(etu)_2(NCS)_2$	2113	787	-	B	63
$Ni(etu)_2(NCS)_2$	2128	777	-	B	63
$Ni(etu)_4(NCS)_2$	2060	790	-	N	83
$Ni(tam)_2(NCS)_2$	2118	779	466	B	87
$Co(py)_2(NCS)_2$	2099	787	468,472	B	88
$Co(py)_4(NCS)_2$	2072	801	478,481	N	88
$Ni(py)_2(NCS)_2$	2100	782	466,474	B	88
$Ni(py)_4(NCS)_2$	2079	800	478,483	N	88

[a] Nitrogen bonded (N) or M-NCS-M bridged (B)

[b] obscured by ν(As-O).

[c] This work.

donation from the oxygen atom and a subsequent increased reduction in the π component of the As-O bond.

Thiocyanate Complexes

Trimethylarsine oxide reacts with cobalt(II) and nickel(II) thiocyanates to form complexes of the type $M(Me_3AsO)_2(NCS)_2$. The similarity in the band profiles of the ν(As-O) absorptions in the infrared spectra of the $M(Me_3AsO)_2(NCS)_2$ and $M(Me_3AsO)_2X_2$ (X = Cl and Br) (Figure 7), indicates that the Me_3AsO is also acting as a bridging group in the thiocyanate complexes. The electronic spectra of the thiocyanate complexes (Table 12) are typical of high-spin octahedral compounds and similar to those observed for the corresponding halide complexes, although bands are displaced to higher energies due to the increased ligand field strength caused by the introduction of the thiocyanate group.

Confirmation that the thiocyanate must therefore be unidentate is obtained from the thiocyanate infrared frequencies. Although in the arsine oxide complexes ν(C-S) is obscured by ν(As-O), it can be observed in the analogous phosphine oxide complex

$Ni(Me_3PO)_2(NCS)_2$. The similarity in the electronic spectra of $Ni(Me_3AsO)_2(NCS)_2$ and $Ni(Me_3PO)_2(NCS)_2$ indicates that they must have similar structures (Table 12).

The ν(C-N), ν(C-S) and ν(NCS) frequencies, which occur at 2070 - 2090, 807, and 480 cm^{-1} in the spectra of the $ML_2(NCS)_2$ oxo-complexes (Table 16) lie in the range generally expected for nitrogen bonded thiocyanates. For sulphur bonded thiocyanates ν(C-S) and ν(NCS) occur at lower frequencies (690 - 740 and 400 - 450 cm^{-1} respectively[63,64,85]). While it is more difficult to differentiate between M-NCS and M-NCS-M thiocyanate types it appears that the C-N stretching frequencies are usually found below 2100 cm^{-1} for the former and above 2100 cm^{-1} for the latter[86]. The respective C-S ranges for nitrogen bonded and bridged thiocyanate are 790 - 860 and 740 - 790 cm^{-1} [63]. Also included in Table 16, are infrared data for related pyridine and thiourea complexes for which the mode of thiocyanate coordination (N bonded or bridged) has been definitely established. Comparison of the frequencies confirms that the thiocyanate is unidentate in the $M(Me_3AsO)_2(NCS)_2$ octahedral complexes.

Infrared Spectra (500 - 200 cm^{-1}

In accord with the octahedral structures of the $M(Me_3AsO)_2Cl_2$ (M = Fe, Co, Ni) compounds the metal-chlorine stretching vibrations occur between 240 and 260 cm^{-1} [1,2,3]. The corresponding metal-bromine frequencies must lie below 200 cm^{-1}. For the thiocyanate complexes the ν(M-N) absorptions are obscured by ligand bands occurring in the 250 - 300 cm^{-1} region. A band at 259 cm^{-1} is assigned to the metal-thiocyanate mode in the phosphine oxide complex $Ni(Me_3PO)_2(NCS)_2$. Bands assignable to metal-ligand stretching modes occur in the 350 - 400 cm^{-1} range. The ν(M-O) absorptions generally consist of a strong band with a weak shoulder at lower energies. For a structure in which successive metal atoms are bridged by pairs of oxygen atoms, two metal-oxygen infrared bands would be expected[89]. The observation of one ν(M-Cl) band (although another could possibly occur below 200 cm^{-1}) is consistent with a trans arrangement of chlorine atoms. As has been observed in other systems[20,90] the ν(Ni-O) and ν(Ni-Cl) frequencies are higher than the analogous vibration frequencies for the cobalt and iron complexes.

The metal-halogen, metal-thiocyanate and metal-

oxygen stretching vibration bands do not appear to be of value in indicating whether the groups concerned are terminal or bridging. The octahedral polymeric Mpy_2Cl_2 (M = Fe, Co, Ni) complexes could be regarded as reference chlorine-bridged compounds. However, the ν(M-Cl) and ν(M-N) bands which occur in the 200 - 250 cm^{-1} region[90], overlap. The spectra of a number of complexes containing bridged (M-NCS-M) or unidentate (M-NCS) have been reported, but for the same metal the difference in the bridging and terminal ν(M-N) frequencies is insignificant[88]. Comparison of metal-oxygen frequencies for related bridged and terminal systems is complicated by the ν(M-O) modes not being pure. However both the metal-oxygen and metal-halogen modes show the usual variations with coordination number[1,2]. Table 17 lists the ν(M-X) and ν(M-O) frequencies for the octahedral and tetrahedral isomers of $Co(Me_3AsO)_2X_2$. Both frequencies are displaced to lower energies as the coordination number is increased from four to six.

TABLE 17

Low Frequency Infrared Spectral Data (cm^{-1}) for

$Co(Me_3AsO)_2X_2$ Complexes

Complex	ν(Co-O)	ν(Co-X)
tet-$Co(Me_3AsO)_2Cl_2$	429	296, 280
oct-$Co(Me_3AsO)_2Cl_2$	400, 355sh	241
tet-$Co(Me_3AsO)_2Br_2$	427	234, 222
oct-$Co(Me_3AsO)_2Br_2$	399, 355sh	<200

Trimethylarsine Sulphide Complexes

Trimethylarsine sulphide reacts directly with the divalent perchlorates and halides of iron and nickel, giving complexes of the type $[M(Me_3AsS)_4](ClO_4)_2$ and $M(Me_3AsS)_2X_2$ (X = Cl, Br). The iron(II) perchlorate complex shows no tendency to be oxidised by air and the halides are only oxidised slowly. The complex $Ni(Me_3AsS)_2Cl_2$ is difficult to isolate since the mono-adduct $Ni(Me_3AsS)Cl_2$ crystallises preferentially, even from solutions containing a large excess of arsine sulphide. Trimethylarsine sulphide complexes with manganese(II) perchlorate, as evidenced by the lowering of the ν(As-S) frequency, but unreacted components could not be eliminated from the product. With copper(II) salts and trimethylarsine sulphide, immediate reduction to copper(I) occurs (p.113).

X-ray powder photographs show the compounds $Fe(Me_3AsS)_2Cl_2$ and $Ni(Me_3AsS)_2X_2$ (X = Cl,Br) to be isomorphous to the analogous tetrahedral cobalt compounds $Co(Me_3AsS)_2X_2$. The similarity of the powder photographs of the perchlorate complexes $[M(Me_3AsS)_4](ClO_4)_2$ (M = Fe, Ni) suggests that they have the same basic structure.

TABLE 18

Electronic Spectra of Tetrahedral Fe(II) and Ni(II) Complexes[a]

Compound	State	
$[Fe(Me_3AsS)_4](ClO_4)_2$	refl.	5,700(br)
	KBr	5,600(br)
$Fe(Me_3AsS)_2Cl_2$	refl.	~4,300 (br)
$Fe(Me_3AsS)_2Br_2$	refl.	~4,300 (br)
$[Ni(Me_3AsS)_4](ClO_4)_2$	$MeNO_2$	14,450(214), 13,260(200), 10,800(w sh), 8,400(18)
	refl.	21,300[c], 14,950, 13,900, 11,500, 8,200, 4,600
$Ni(Me_3AsS)_2Cl_2$	$MeNO_2$[b]	15,900(sh), 15,270(173), 13,970(173), 10,200(w sh), 8,930(44)
	refl.	24,900[c], 14,800(br), 10,200(sh), 8,900
$Ni(Me_3AsS)_2Br_2$	$MeNO_2$	14,990(199), 13,700(s sh), 9,850(w sh), 8,900(59)
	refl.	22,900[c], 14,500, 13,600(s sh), 9,500(w sh), 8,800, 4,300
$Ni(Me_3AsS)Cl_2$[d]	refl.	21,700, 12,500, 11,000(sh), 7,500(br).

[a] Molar extinction coefficients in parentheses

[b] Plus excess ligand

[c] Shoulder on charge transfer band

[d] Octahedral complex

Electronic Spectra

The rapid oxidation in solution of the iron(II) compounds prevents the measurement of their solution spectra. For the nickel(II) complexes solution and reflectance spectra are similar, although for the relatively unstable $Ni(Me_3AsS)_2Cl_2$ complex which shows ligand dissociation in solution, free ligand was added to restore band intensities to their maximum values.

The electronic spectra of the $[M(Me_3AsS)_4](ClO_4)_2$ and $M(Me_3AsS)_2X_2$ (X = Cl,Br) complexes are typical of tetrahedral iron(II)[91] and nickel(II)[92] compounds. (Table 18 and Figures 3,5) The reflectance spectra of the iron complexes show one broad band, at 5700 cm^{-1} for the perchlorate and about 4300 cm^{-1} for the halides (Table 18). As expected for tetrahedral iron(II), the absorptions occur in the near-infrared region and can be assigned to the $^5E \rightarrow {}^5T_2$ transition, which corresponds to Δ, the ligand field strength parameter[73,91].

The intensities and energies of the electronic spectral bands of $[Ni(Me_3AsS)_4](ClO_4)_2$ and $Ni(Me_3AsS)_2X_2$ are indicative of tetrahedral coordination. The bands at 13,000 - 15,000 cm^{-1} (ϵ = 170 - 220) may be

assigned to the $^3T_1(F) \longrightarrow {}^3T_1(P)$, ($\nu_3$) transition while those at 8000 - 9000 cm^{-1} (ϵ = 18 - 60) to the $^3T_1(F) \longrightarrow {}^3A_2(F)$, ($\nu_2$) transition (Figure 8). Bands at about 4500 cm^{-1} can probably be assigned to the $^3T_1(F) \longrightarrow {}^3T_2(F)$, ($\nu_1$) transition[79,92]. The ratio of the ν_3 to ν_2 band intensities for $[Ni(Me_3AsS)_4](ClO_4)_2$ is about 12 and decreases to 3 - 4 for the halides. In regular tetrahedral nickel complexes, ν_3 is usually 10 - 20 times more intense than ν_2[92]. This is in agreement with the fact that in a strong field limit ν_3 remains a one electron transition while ν_2 becomes a two electron transition. However, with the introduction of low-symmetry components of the ligand field, as in the $Ni(Me_3AsS)_2X_2$ complexes, the intensity of ν_2 relative to ν_3 increases[93].

The electronic reflectance spectrum of $Ni(Me_3AsS)Cl_2$ indicates that it has an essentially octahedral structure. The three main bands at 7,500, 12,500 and 21,700 cm^{-1} can therefore be assigned to the $^3A_{2g} \longrightarrow {}^3T_{2g}$, $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ transitions respectively[72,77].

Electronic Spectral Parameters

The effects of spin-orbit coupling are more important in tetrahedral nickel(II) complexes than

in cobalt(II) or iron(II) complexes[73]. Thus Goodgame et al[92] found that calculations using the Tanabe and Sugano matrices[39], in which spin-orbit coupling is ignored, gave unlikely Δ values. The ligand field parameters for $[Ni(Me_3AsS)_4](ClO_4)_2$ have therefore been calculated using the matrices of Liehr and Ballhausen[94], which include the spin-orbit parameter, λ. The parameters were adjusted using a computer (Appendix II) until reasonable agreement between the observed spectra and the calculated energy levels was obtained (Table 19). The values of Δ and B' so obtained were 4110 cm^{-1} and 670 cm^{-1} respectively. The low B' value is in agreement with that obtained for the analogous cobalt complex $[Co(Me_3AsS)_4](ClO_4)_2$ (Table 20).

The calculations indicate that the observed splitting of the $^3T_1(F) \longrightarrow {}^3T_1(P)$, ($\nu_3$) absorption (1190 cm^{-1}) is greater than that predicted ($\sim$ 550 cm^{-1}) on the basis of spin-orbit coupling alone and that the weak shoulder at 10,800 cm^{-1} can be assigned to spin-forbidden transitions to components of the ^1D state. Transitions to components of the ^1G state appear to be obscured by the ν_3 band and by a charge transfer band.

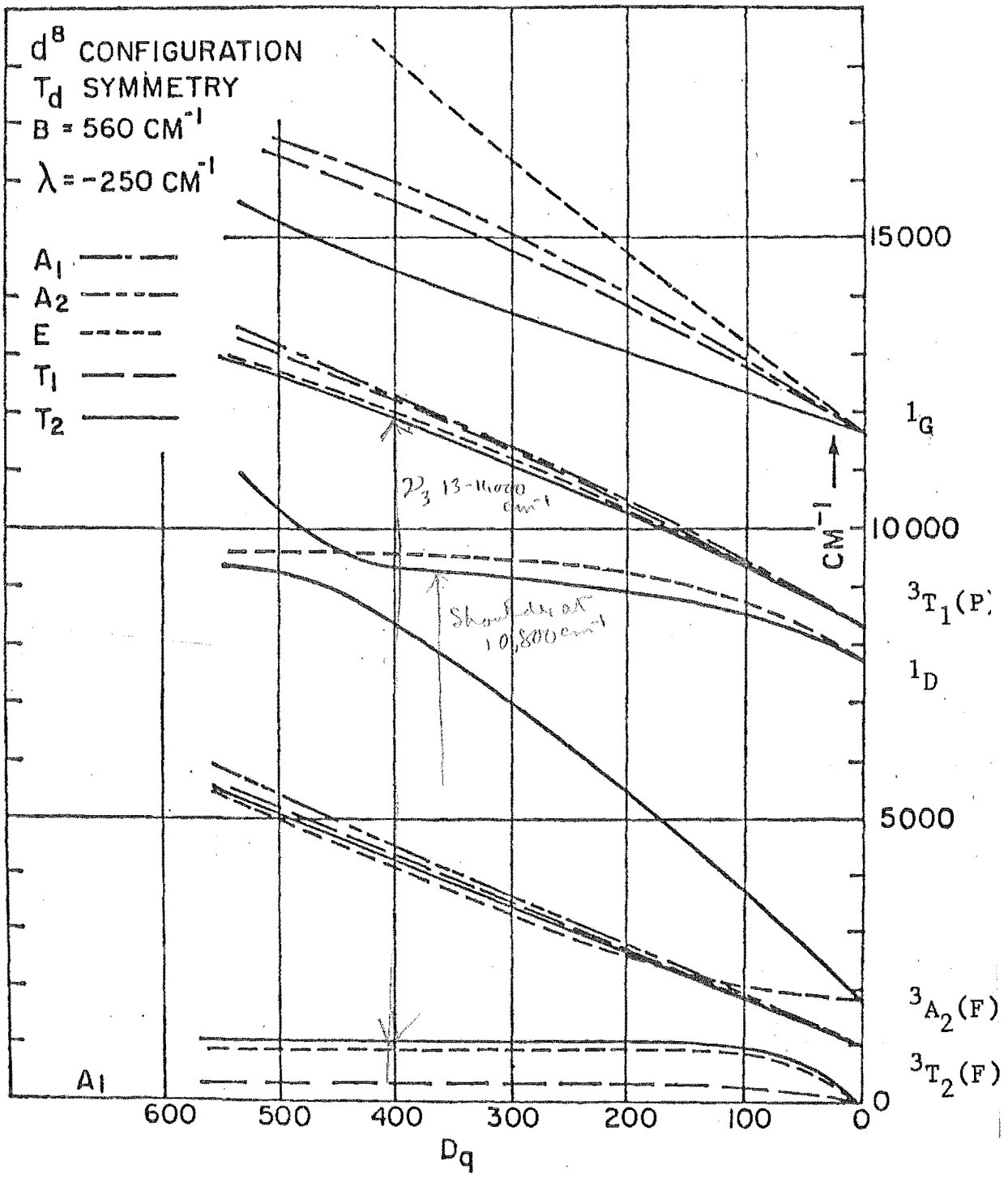


FIGURE 8. Calculated energy levels for Ni(II) in a tetrahedral field with spin-orbit coupling. (ref. 95).

TABLE 19

Comparison of observed and calculated electronic spectra for $[Ni(Me_3AsS)_4](ClO_4)_2$ with $\Delta = 4110$, $B' = 674$ and $\lambda = -250\ cm^{-1}$

Observed[a] (cm^{-1})	Calculated (cm^{-1})	Assignment of Upper level[b]
	4,177	$^3T_2(F)$
	4,249	
	4,298	
	4,499	
8,400	8,396	$^3A_2(F)$
	10,287	$^1T_2(D)$
10,800	10,655	$^1E(D)$
13,260	13,600	$^3T_1(P)$
	13,649	
	13,985	
14,450	14,154	
	16,116	$^1T_2(G)$
	17,573	$^1T_1(G)$
	17,592	$^1A_1(G)$
	19,704	$^1E(G)$

[a] Solution spectra

[b] See Figure 8.

TABLE 20

Electronic Spectral Parameters for the tetrahedral $[M(Me_3AsS)_4]^{2+}$ Complexes

Complex	Δ (cm^{-1})	B' (cm^{-1})	β [a]
$[Fe(Me_3AsS)_4](ClO_4)_2$	5,700	-	-
$[Co(Me_3AsS)_4](ClO_4)_2$	4,070	600	0.62
$[Ni(Me_3AsS)_4](ClO_4)_2$	4,110	670	0.64

[a] $\beta = B'/B$, B is taken to be 967 and 1056 cm^{-1} for the free Co and Ni ions respectively.

TABLE 21

Magnetic Data for Tetrahedral Fe(II) and Ni(II) Complexes

Compound	T (^{o}K)	χ_m(X10^3) (cgsu)	χ_m^{corr}(X10^3) (cgsu) [a]	μ (B.M)
$[Fe(Me_3AsS)_4](ClO_4)_2$	293	10.56	11.03	5.10
$Fe(Me_3AsS)_2Br_2$	291	10.80	11.07	5.10
$[Ni(Me_3AsS)_4](ClO_4)_2$	293	4.04	4.51	3.27
$Ni(Me_3AsS)_2Br_2$	293	4.67	4.94	3.42
$Ni(Me_3AsS)Cl_2$ [b]	294	4.71	4.86	3.39

[a] Corrected for diamagnetism

[b] Octahedral complex

Magnetic Susceptibilities

The magnetic moments of $[Fe(Me_3AsS)_4](ClO_4)_2$ and $[Ni(Me_3AsS)_4](ClO_4)_2$ are 5.10 B.M. and 3.27 B.M. respectively. Both these values lie below the ranges generally observed for tetrahedral iron(II) (5.2 - 5.4 B.M.[96]) and nickel(II) (3.5 - 4.2 B.M.[78,79]). However, distortions from tetrahedral symmetry and delocalisation of the d electrons will tend to reduce the magnetic moments[73,96,97]. The low β value observed for the nickel complex suggests that the low moments can be related to the effects of metal-ligand covalency.

Infrared Spectra

Apart from a reduction in the ν(As-S) frequency, the main ligand bands are not significantly displaced upon coordination. The perchlorates show strong single absorptions at 1100 and 624 cm^{-1}, consistent with the presence of the uncoordinated perchlorate anion[59]. The ν(As-S) absorptions for tetrahedral $Ni(Me_3AsS)_2Cl_2$ and octahedral $Ni(Me_3AsS)Cl_2$ both occur at 444 cm^{-1}, suggesting that the latter complex contains unidentate rather than bridging arsine sulphide groups (see p.51). Therefore, as postulated

for the analogous pyridine complex $NipyCl_2$[98], polymerisation is probably achieved through bridging chlorine atoms.

As for the cobalt complexes (Table 8), bands in the 264 - 311 cm^{-1} region of the spectra of the tetrahedral iron and nickel complexes (Table 22) can be assigned to metal-ligand stretching vibrations. The anomalous solid state spectrum (500 - 200 cm^{-1}) of $[Ni(Me_3AsS)_4](ClO_4)_2$ could arise from the coupling of a lattice mode with ν(M-S), since in solution the spectrum is similar to those observed for the other tetrahedral $[M(Me_3AsS)_4]^{2+}$ complexes (Table 23). Electronic spectra indicate that the complex has a tetrahedral structure in both the solution and in the solid state (Table 18). The observation of two ν(M-S) bands for the $[M(Me_3AsS)_4](ClO_4)_2$ complexes can probably be related to the non-linearity of the M-S-As linkage (see p.32). For the chloride complexes, ν(M-Cl) and ν(M-S) occur at similar frequencies, thus preventing their separate assignment. However, ν(M-Br) are found below ν(M-S) for the bromides, in the range (200 - 250 cm^{-1}) generally expected for tetrahedral complexes[2,3].

Table 23 lists the ν(M-S) frequencies for the

TABLE 22

Infrared Spectra of Tetrahedral Fe(II) and Ni(II) Trimethylarsine Sulphide Complexes (cm^{-1}) [a]

Compound	ν(As-S)	ν(M-S)	ν(M-X)
$[Fe(Me_3AsS)_4](ClO_4)_2$	429s	310mw 290m	-
$Fe(Me_3AsS)_2Cl_2$	440s	(318s, 299s, 268m, 259m) [b]	
$Fe(Me_3AsS)_2Br_2$	439s	284m, 264mw	245m
$[Ni(Me_3AsS)_4](ClO_4)_2$	438s, 430s	342m, 282m, 274m	-
	445s, 438s	311m, 292m [c]	-
$Ni(Me_3AsS)_2Cl_2$	444s	(320m, 302s, 288s, 272sh) [b]	
$Ni(Me_3AsS)_2Br_2$	445s	311m, 290m,	233s, 225sh
$Ni(Me_3AsS)Cl_2$ [d]	444s	(250s, 223m) [b]	

[a] As Nujol mulls

[b] ν(M-S) + ν(M-Cl)

[c] Values for nitromethane solution

[d] Octahedral complex.

TABLE 23

ν(M-S) Frequencies for $[M(Me_3AsS)_4](ClO_4)_2$ complexes[a]

Complex	ν(M-S)
$[Fe(Me_3AsS)_4](ClO_4)_2$	310, 290
$[Co(Me_3AsS)_4](ClO_4)_2$	312, 294
	(312, 295)
$[Ni(Me_3AsS)_4](ClO_4)_2$	342, 282, 274[b]
	(311, 292)
$[Zn(Me_3AsS)_4](ClO_4)_2$	287
	(289, 277 sh)

[a] Values for nitromethane solutions in parentheses.

[b] Anomalous spectrum (see text).

$[M(Me_3AsS)_4]^{2+}$ (M = Fe, Co, Ni and Zn) series of complexes. Apart from the lower values for the zinc complex, there appears to be no significant difference in the ν(M-S) frequencies. In contrast, in the MX_4^{2-} anions, the ν(M-X) frequencies follow the order[62], Fe < Co > Ni > Zn, which is the order of the tetrahedral ligand field stabilization energies. Undoubtedly the situation is complicated in the arsine sulphide complexes by the ν(M-S) vibrational modes not being pure. The metal-sulphur stretching frequencies (330 - 264 cm^{-1}) observed in the present work lie well within the range observed for these modes in an increasing number of monodentate thio-ligand complexes (350 - 200 cm^{-1})[61,87,99,100,101].

Comparison of Me_3AsO and Me_3AsS Halide Complexes

The particular complex isolated from a reaction system depends on a number of factors such as steric and electronic effects, ligand polarizability and crystal packing. The formation of tetrahedral complexes is considered to be favoured by large, easily polarized ligands and by a metal ion which has a symmetrical shell of non-bonding d electrons in a tetrahedral field (i.e. d^7 and d^{10})[102,103]. Thus the sulphide ligand gives tetrahedral complexes, $M(Me_3AsS)_2X_2$ (Table 11), although special structural factors can

intervene as must be the case with octahedral $Ni(Me_3AsS)Cl_2$. With the presumably less polarizable oxo-ligand, the stereochemistry of the $M(Me_3AsO)_2X_2$ complex appears to be more dependent on the metal atom, both tetrahedral and bridged octahedral complexes being isolated (Table 24).

The formation of octahedral and tetrahedral isomers is not common although the pyridine complex $Co(py)_2Cl_2$ is known to exist as either an octahedral polymer with bridged chlorines, or as a tetrahedral monomer. The tetrahedral form is stable in solution but gradually reverts to the octahedral form in the crystalline state[102]. With cobalt bromide only tetrahedral $Co(py)_2Br_2$ has been isolated[102]. In contrast both the $Co(Me_3AsO)_2Cl_2$ isomers are stable in the solid state, and both an unstable octahedral as well as a stable tetrahedral isomer of $Co(Me_3AsO)_2Br_2$ exists. Only an octahedral form of $Co(Me_3AsO)_2(NCS)_2$ could be isolated.

The bridged octahedral complexes $Co(Me_3AsO)_2X_2$ (where X = NCS, Cl, and Br) all dissolve in nitromethane to give tetrahedral monomers, indicating that solid state effects must be important in stabilizing the polymeric $M(Me_3AsO)_2X_2$ compounds.

TABLE 24

$M(Me_3AsO)_2X_2$ Complexes

Complex	Structure[a]	Comment
$Fe(Me_3AsO)_2X_2$	bri. oct.	oxidised in $MeNO_2$
$Co(Me_3AsO)_2Cl_2$	bri. oct.	solid stable, tetrahedral in $MeNO_2$
	tetr.	stable in solid and solution
$Co(Me_3AsO)_2Br_2$	bri. oct.	solid rapidly converts to tetrahedral isomer in air, tetrahedral in $MeNO_2$
	tetr.	stable isomer
$Ni(Me_3AsO)_2X_2$ (X = Cl,Br)	bri. oct.	insoluble in common solvents
$Zn(Me_3AsO)_2X_2$ (X = Cl, Br)	tetr.	

[a] All bridged octahedral complexes isomorphous, all tetrahedral complexes isomorphous.

CHAPTER 3

HIGH-SPIN FIVE-COORDINATE $[ML_5]^{2+}$ AND $[ML_4(ClO_4)]^{+}$ COMPLEXES WITH TRIMETHYLARSINE OXIDE

INTRODUCTION

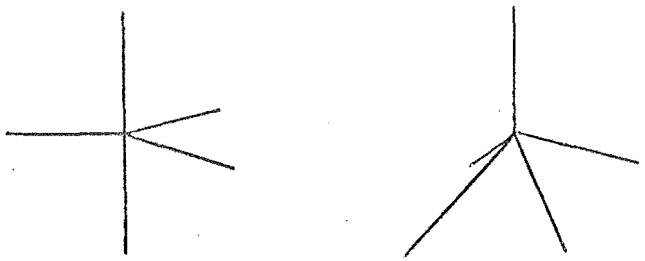
Although examples of five-coordinate first row transition metal complexes with polydentate ligands are becoming increasingly common, examples of corresponding complexes with monodentate ligands are few and ML_5 complexes with identical ligands are limited to low-spin species such as $Fe(CO)_5$ [104], $[Co(CNCH_3)_5]^{+}$ [105], $[Ni(P(OCH)_3(CH_2)_3)_5]^{2+}$ [106], and $[Ni(CN)_5]^{3-}$ [107], and $[CuCl_5]^{3-}$ [108] which has a d^9 configuration. In this chapter the first high-spin $[ML_5]^{2+}$ complexes of divalent manganese, cobalt and nickel have been prepared with trimethylarsine oxide and their spectroscopic and magnetic properties investigated. A related series of $[ML_4(ClO_4)]^{+}$ complexes (M = Mn,Fe,Ni and Cu) are also described.

The two idealized geometries of five-coordination, the trigonal bipyramid and the square pyramid (Figure 9a), practically never occur. In the case of the ML_5 trigonal bipyramidal complexes $[Co(CNCH_3)_5]^{+}$, $[Ni(P(OCH)_3(CH_2)_3)_5]^{2+}$, $[Ni(CN)_5]^{3-}$ and $[CuCl_5]^{3-}$, the axial bonds are shorter than equatorial bonds [105-108]. In square pyramidal complexes of transition elements the axial bond is normally longer than the

equatorial bonds and the metal atom lies above the basal plane. C_{4v} symmetry is closely attained in $[Ni(CN)_5]^{3-}$ [107] and $[Co(Ph_2MeAsO)_4(ClO_4)]^{+}$ [109]. There are many examples of distorted trigonal bipyramidal and distorted square pyramidal complexes which involve donor atoms of more than one type[110,111]. Because only small changes are required to pass from the trigonal bipyramid to the square pyramid (Figure 9b), intermediate geometries often occur. Examples are $Co(Me_5dien)Cl_2$ [112] and $Co(Et_4dien)Cl_2$ [113], (Me_5dien = bis(2-dimethylaminoethyl)methylamine and Et_4dien = bis(2-diethylaminoethyl)amine).

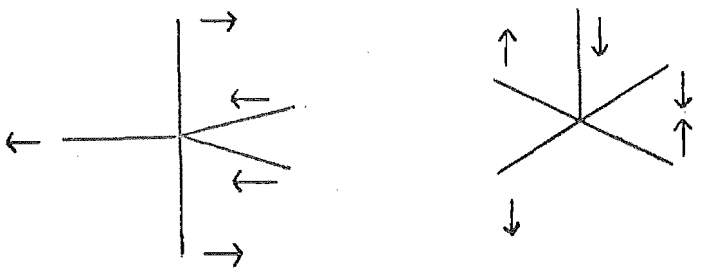
The actual geometry that is observed for a five coordinate complex depends on a number of factors such as repulsions between bonding electron pairs, ligand field stabilization effects, steric requirements of the ligands and packing requirements of the crystal. On the basis of electron pair repulsions it can be shown[114] that a trigonal bipyramid is slightly more stable than the most favourable square pyramid. Irrespective of the d electron configuration (d^1 - d^9), the calculated ligand field stabilization energies favour the square pyramidal structure rather than the trigonal bipyramid[114].

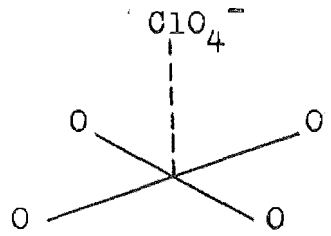
Only a small distortion is required to interconvert the two geometries and the existence of both square pyramidal and trigonal bipyramidal $[Ni(CN)_5]^{3-}$ anions in the same unit cell[107] is indicative of the small energy difference between the two forms. Except for monodentate ligands such as chloride, cyanide and carbonyl, the steric requirements of the ligand probably predominate. Thus $[Co(Me_6trien)Br]^+$ has a trigonal bipyramidal configuration with the bromine in an axial position[115], while $[Ni(5\text{-}Cl\text{-}salen\text{-}NEt_2)]$ is a distorted square pyramid[116]. (Me_6trien = tris(2-dimethylaminoethyl)amine and 5-Cl-salen-NEt_2 = N-β-diethylaminoethyl-5-chlorosalicylaldimine). In fact steric crowding by such polydentate ligands around the metal ion prevents a six-coordinated configuration being attained[117].



a. Trigonal bipyramid (D_{3h}) Square pyramid. (C_{4v})

b. Relationship between D_{3h} and C_{4v}.





c. Distortion towards square planar.

FIGURE 9. Geometries for five-coordinate species

TABLE 25

Five-Coordinate Complexes from Trimethylarsine Oxide(L)

$[ML_5]^{2+}$	$[ML_4(ClO_4)]^+$
$[MnL_5](ClO_4)_2$	$[MnL_4(ClO_4)]ClO_4$
a	$[FeL_4(ClO_4)]ClO_4$ $[FeL_4(ClO_4)]BPH_4$
$[CoL_5](ClO_4)_2$ [b]	a
$[NiL_5](ClO_4)_2$ $[NiL_5](BF_4)_2$ $[NiL_5](NO_3)_2$	$[NiL_4(ClO_4)]ClO_4$ $[NiL_4(ClO_4)]BPh_4$
a	$[CuL_4(ClO_4)]ClO_4$ [c]

[a] Complexes could not be isolated.

[b] Cobalt also forms a tetrahedral $[CoL_4](ClO_4)_2$ complex isomorphous with its zinc analogue (Chapter 1).

[c] A tetraphenylborate could not be prepared.

RESULTS AND DISCUSSION

Under anhydrous conditions, the reaction of trimethylarsine oxide with the divalent perchlorates of the first row transition metals yields a range of $[M(Me_3AsO)_5](ClO_4)_2$ (M = Mn,Co and Ni) and $[M(Me_3AsO)_4(ClO_4)]ClO_4$ (M = Mn,Fe,Ni and Cu) complexes (Table 25). The $[M(Me_3AsO)_5](ClO_4)_2$ compounds are best prepared from acetone using a slight excess of ligand, while the $[M(Me_3AsO)_4(ClO_4)]ClO_4$ complexes are favoured using a deficiency of ligand and ethanol as solvent. Since the compounds are generally sensitive to atmospheric moisture, especially the $[M(Me_3AsO)_4(ClO_4)]ClO_4$ series, they were all handled in a dry box. Infrared spectra were examined to confirm the absence of water. The manganese complexes $[Mn(Me_3AsO)_5](ClO_4)_2$ and $[Mn(Me_3AsO)_4(ClO_4)]ClO_4$ are susceptible to atmospheric oxidation and were therefore prepared and stored under nitrogen. Attempts to isolate $[M(Me_3AsO)_5](ClO_4)_2$ complexes of iron, copper and zinc, using different solvents, temperatures and conditions of crystallization were unsuccessful. With zinc, only $[Zn(Me_3AsO)_4](ClO_4)_2$, isomorphous with its tetrahedral cobalt analogue (p.15) could be isolated. However a lowering of the ν(Zn-O) mode

from 430 cm^{-1} to about 400 cm^{-1}, when excess ligand was added to a nitromethane solution of $[Zn(Me_3AsO)_4](ClO_4)_2$ indicated the development of higher coordination (p.92). The related nitrate and tetrafluoroborate compounds $[Ni(Me_3AsO)_5]X_2$ ($X = NO_3$ and BF_4) were also prepared and the isolation of the tetraphenylborates $[M(Me_3AsO)_4(ClO_4)]BPh_4$ (M = Fe and Ni) and $[Ni(Me_3AsO)_4(NO_3)]BPh_4$ was possible.

X-ray powder photographs show the $[M(Me_3AsO)_5](ClO_4)_2$ (M = Mn, Co and Ni) compounds to be isomorphous. The close similarity of the photographs of the $[M(Me_3AsO)_4(ClO_4)]ClO_4$ (M = Mn, Fe and Ni) series suggests that the complexes have essentially the same structure. The copper complex $[Cu(Me_3AsO)_4(ClO_4)]ClO_4$ gives a similar photograph to those from the other $[M(Me_3AsO)_4(ClO_4)]ClO_4$ complexes although it shows several additional lines. Trimethylphosphine oxide also reacts with the divalent first row transition metals to give a series of five coordinate complexes isomorphous with their arsine oxide analogues[21,131].

Electronic Spectra

The electronic reflectance spectra of the cobalt and nickel $[M(Me_3AsO)_5]X_2$ complexes (Table 26 and

Figure 10) show a marked similarity to the spectra of high spin cobalt(II) and nickel(II) compounds which are known to be five-coordinate[117 - 120]. The spectrum of $[Co(Me_3AsO)_5](ClO_4)_2$ shows a medium band at 11,000 cm^{-1} which distinguishes it from those of tetrahedral and octahedral complexes, (c.f. Figures 4 and 10) while the spectra of the $[Ni(Me_3AsO)_5]X_2$ ($X = ClO_4$, BF_4 and NO_3) differ from those of octahedral complexes by absorptions at about 5,000 cm^{-1} and in the 8,000 - 12,000 cm^{-1} region (c.f. Figures 5 and 10). The spectra of the $[M(Me_3AsO)_5]^{2+}$ (M = Co and Ni) complexes more closely resemble those obtained for other complexes known from X-ray analyses to have a square pyramidal configuration rather than those from complexes of the trigonal bipyramidal class[119]. Molecular models suggest that a square pyramidal structure is favoured due to the steric requirements of the methyl groups. Representative spectra from the present work are shown in Figure 10, along with those of $[Co(Ph_2MeAsO)_4(ClO_4)]ClO_4$ and $[Ni(Ph_2MeAsO)_4(ClO_4)]ClO_4$ which are known to have a basicaly square pyramidal structure[109,121]. Since $[Mn(Me_3AsO)_5](ClO_4)_2$ is isomorphous to the corresponding cobalt and nickel complexes it must also have a five-

coordinate structure.

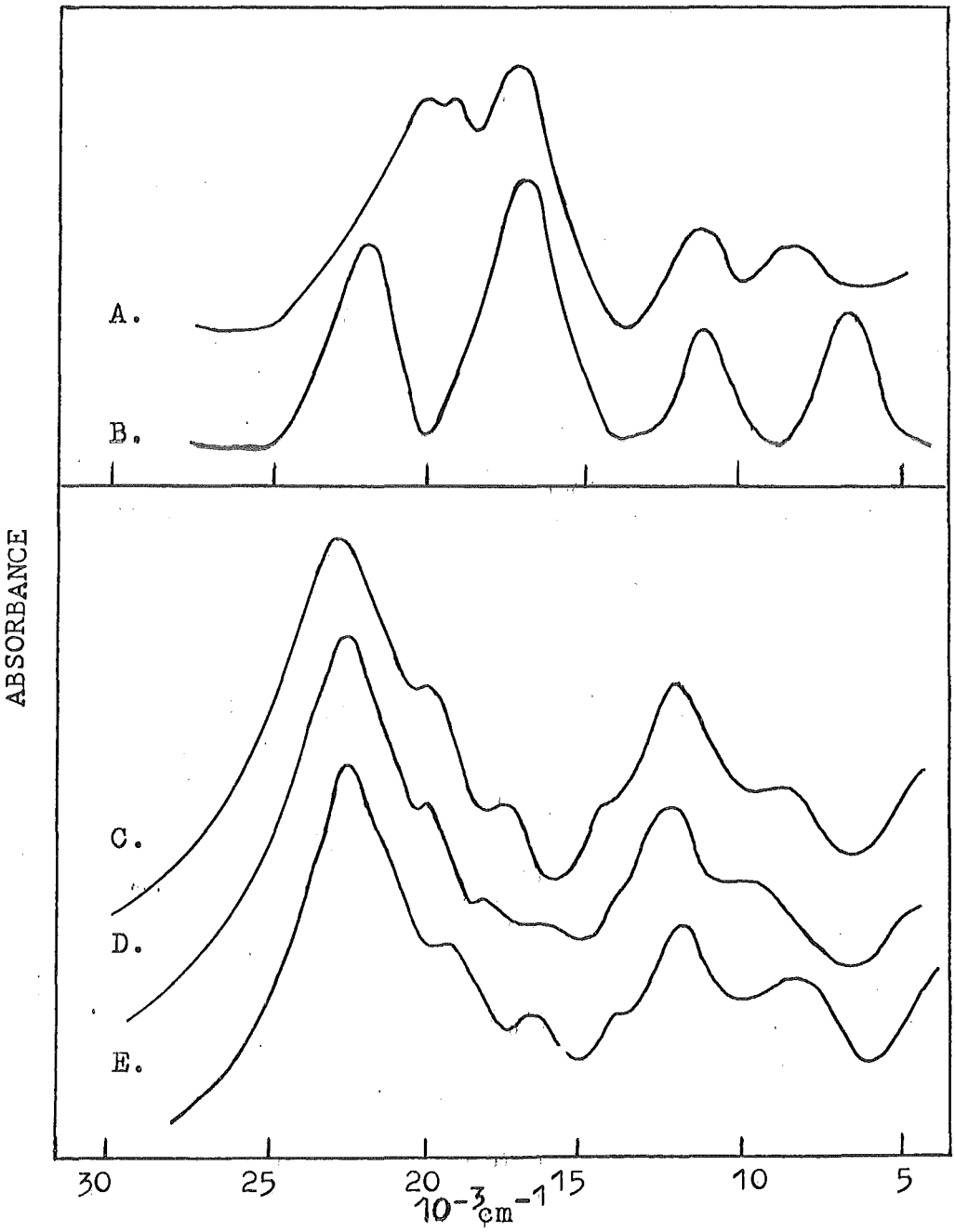
The same basic structure is suggested for the $[M(Me_3AsO)_4(ClO_4)]X$ ($X = ClO_4$ or BPh_4) complexes. The spectra of $[Ni(Me_3AsO)_4(ClO_4)]ClO_4$ and $[Ni(Me_3AsO)_4(ClO_4)]BPh_4$ are very similar to that of $[Ni(Me_3AsO)_5](ClO_4)_2$ (Figure 10) and the manganese(II) and iron(II) compounds can reliably be formulated in the same manner in view of the close similarity of their powder photographs to that of $[Ni(Me_3AsO)_4(ClO_4)]ClO_4$. The isolation of the tetraphenylborates of iron(II) and nickel(II) in itself provides evidence for this formulation (Table 25).

Both the free cobalt(II) and nickel(II) ions have an F ground term and some 15,000 cm^{-1} above it a P term[73]. In a square pyramidal (C_{4v}) ligand field the F term splits into the states A_2, B_1, B_2, E and E while the P term is split into A_2 and E[123]. The relative energies of these states have been estimated for nickel(II)[123] but not for cobalt(II), although the corresponding calculations for both nickel(II)[123] and cobalt(II)[117] in a trigonal bipyramidal field (D_{3h}) have been carried out. Since it appears that the complexes described in the present work more closely approach C_{4v} symmetry than D_{3h}, detailed

assignment of the spectral bands has not been attempted. However the strong bands in the 17,000 - 19,600 cm^{-1} region in the spectrum of $[Co(Me_3AsO)_5](ClO_4)_2$ can be correlated with the $^4F \rightarrow {}^4P$ free ion transition and the medium bands at 8,500 and 11,000 cm^{-1} to transitions from the ground state component of the ^4F term to higher energy components of the term. Similarly for the nickel complexes the strong bands at about 22,000 cm^{-1} may be correlated with the $^3F \rightarrow {}^3P$ free ion transitions and the lower energy medium strength bands at 8,000 - 13,000 cm^{-1} to ^3F intraterm transitions. A similar situation occurs for tetrahedral cobalt(II) and nickel(II) complexes where the intense band in the visible region is always correlated with the $^4F \rightarrow {}^4P$ and $^3F \rightarrow {}^3P$ free ion transitions respectively[124].

The spectrum of $[Ni(Me_3AsO)_4(NO_3)]BPh_4$ is significantly different from that of the five coordinate $[Ni(Me_3AsO)_4(ClO_4)]BPh_4$ complex (Table 26). The spectrum however is characteristic of nickel in an octahedral field and therefore establishes that the nitrate is functioning as a bidentate ligand. Accordingly the bands, which occur at 7,200, 12,300 and 23,400 cm^{-1} can be assigned[72] to the $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ spin-allowed

FIGURE 10. Reflectance spectra of five-coordinate complexes.



A = $[Co(Me_3AsO)_5](ClO_4)_2$; B = $[Co(Ph_2MeAsO)_4(ClO_4)]$ ClO_4; C = $[Ni(Me_3AsO)_5](ClO_4)_2$; D = $[Ni(Me_3AsO)_4(ClO_4)]ClO_4$; E = $[Ni(Ph_2MeAsO)_4(ClO_4)]$ ClO_4.

TABLE 26

Band Maxima for Diffuse Reflectance Spectra of Five-coordinate Complexes (cm^{-1})

$[Fe(Me_3AsO)_4(ClO_4)]ClO_4$	11,000w br
$[Co(Me_3AsO)_5](ClO_4)_2$	19,600s, 18,700s, 17,000s, 11,000m, 8.500m br
$[Ni(Me_3AsO)_5](ClO_4)_2$	22,200s, 19,200m, 17,150w, 13,600sh, 11,300m, 8,600w br[a]
	22,200(120), 19,200sh, 17,200sh, 13,600(5), 11,300(20), 8,600sh[b]
$[Ni(Me_3AsO)_5](BF_4)_2$	22,100s, 19,100m, 17,150w, 13,500sh, 11,300m, 8,700w br[a]
$[Ni(Me_3AsO)_5](NO_3)_2$	22,200s, 19,100m, 17,150w, 13,550sh, 11,300m, 8,600w br[a]
$[Ni(Me_3AsO)_4(ClO_4)]ClO_4$	22,300s, 19,400m, 17,200sh, 15,600w, 13,500sh, 11,200m 8,600w br[a]
$[Ni(Me_3AsO)_4(ClO_4)]BPh_4$	22,300s, 19,400sh, 17,200sh, 15,400w, 13,400sh, 11,300m, 8,600w br[a]
$[Ni(Me_3AsO)_4(NO_3)]BPh_4$[c]	23,400m, 13,700sh, 12,300m, 7,200w br
$[Cu(Me_3AsO)_4(ClO_4)]ClO_4$	17,000sh, 14,500m br

[a] For the five-coordinate nickel complexes there is also evidence of a band with maximum below 5,000 cm^{-1}.

[b] Acetone solution (2.16×10^{-3}M), with molar extinction coefficients in parentheses.

[c] Octahedral complex.

TABLE 27

Magnetic Data for Five-Coordinate Complexes

Compound	T (^{o}K)	χ_m (X10^3) (cgsu)	χ_m^{corr} (X10^3) (cgsu) [a]	μ (B.M.)
$[Mn(Me_3AsO)_5](ClO_4)_2$	294	14.93	15.46	6.05
$[Fe(Me_3AsO)_4(ClO_4)]ClO_4$	292	9.93	10.36	4.94
$[Co(Me_3AsO)_5](ClO_4)_2$	296	9.13	9.65	4.80
$[Ni(Me_3AsO)_5](ClO_4)_2$	296	4.97	5.49	3.62
$[Ni(Me_3AsO)_5](BF_4)_2$	293	5.04	5.58	3.63
$[Ni(Me_3AsO)_4(ClO_4)]ClO_4$	296	4.88	5.32	3.56
$[Cu(Me_3AsO)_4(ClO_4)]ClO_4$	291	1.30	1.73	2.02

[a] Corrected for diamagnetism.

transitions respectively.

Magnetic Susceptibilities

The magnetic moments (Table 27) show that all the complexes are of the high-spin type, the values lying within the ranges observed for other high-spin five-coordinate complexes. The value for $[Co(Me_3AsO)_5](ClO_4)_2$ (4.80 B.M.) is greater than that found for the corresponding tetrahedral complex $[Co(Me_3AsO)_4](ClO_4)_2$ (4.66 B.M.), while those observed for the nickel complexes ($\sim$3.6 B.M.) lie above the range usually expected for octahedral nickel(II) (2.9 - 3.4 B.M.[78]).

Infrared Spectra

The infrared spectra of $[Mn(Me_3AsO)_5](ClO_4)_2$, $[Co(Me_3AsO)_5](ClO_4)_2$ and $[Ni(Me_3AsO)_5]X_2$ (where X = ClO_4, BF_4 and NO_3) are consistent with the presence of the uncoordinated anions. The free perchlorate ion belongs to the point group T_d and only two fundamentals, $\nu_3(T_2)$ and $\nu_4(T_2)$, are expected to be observed in the infrared[59]. Thus the $[M(Me_3AsO)_5](ClO_4)_2$ compounds show strong single bands at 1,100 cm^{-1} (ν_3) and 624 cm^{-1} (ν_4). A

similar situation would be expected for the tetrahedral tetrafluoroborate anion but in $[Ni(Me_3AsO)_5](BF_4)_2$ the ν_3 absorption has two components at 1095 and 1050 cm^{-1}. However the splitting has been shown to be due to the presence of both $^{10}BF_4^-$ and $^{11}BF_4^-$ [125,126]. In a complex containing 96% ^{10}B (as uncoordinated $^{10}BF_4^-$) the 1050 cm^{-1} component almost disappeared[126]. In $[Ni(Me_3AsO)_5](NO_3)_2$ the ν_3 (E') absorption occurs at 1350 cm^{-1}, consistent with the presence of ionic nitrate (D_{3h} symmetry)[127].

When the perchlorate anion coordinates as a unidentate ligand its symmetry is lowered to C_{3v} and a splitting of the degenerate modes is usually observed[59,121]. Therefore in the $[M(Me_3AsO)_4(ClO_4)]ClO_4$ (M = Mn, Fe, Ni and Cu) complexes three bands arising from the ν_3 (T_2) mode could be expected in the 1100 cm^{-1} region, indicating the presence of both coordinated and ionic perchlorate groups. Although the ν_3 absorption is broad there is no conspicuous splitting even at 77°K. In the tetraphenylborate complexes $[M(Me_3AsO)_4(ClO_4)]BPh_4$ (M = Fe and Ni) a shoulder does appear at 1065 cm^{-1}. However it is recognised that this is not a reliable criterion for

anion coordination since such coordination has been established for a number of compounds which do not show splitting of anion absorptions [128-130]. On the other hand, correlations between the degree of splitting and the strength of coordination have been made[128] and on this basis the lack of splitting for these complexes indicates a weak association of perchlorate.

In contrast the anion absorptions in $[Ni(Me_3AsO)_4(NO_3)]BPh_4$ definitely indicate nitrate coordination. On lowering the symmetry of the nitrate group from D_{3h} to C_{2v} the $\nu_1(A_1)$ mode becomes infrared active and the $\nu_3(E')$ splits [127]. In $[Ni(Me_3AsO)_4(NO_3)]BPh_4$ the nitrate absorption bands occur at 1029 (ν_1), 1480 and 1295 (ν_3), and 800 cm^{-1} (ν_2). From infrared data alone, it is not possible to distinguish between unidentate or bidentate nitrate[127].

In the five-coordinate complexes the ν(As-O) absorption generally occurs in the 855 - 869 cm^{-1} region. For the octahedral complex, $[Ni(Me_3AsO)_2(NO_3)]BPh_4$ the ν(As-O) absorptions are found at higher frequencies (880, 866 cm^{-1}) (Table 28). A weak methyl deformation mode at about 840 cm^{-1} does not interfere with the

TABLE 29

ν(M-O) Frequencies for $[CoL_4]^{2+}$ and $[CoL_5]^{2+}$ Complexes

Complex	ν(M-O)
$[Co(Me_3AsO)_4](ClO_4)_2$	442, 428
$[Co(Me_3AsO)_5](ClO_4)_2$	407, 391
$[Co(Me_3PO)_4](ClO_4)_2$	460, 448
$[Co(Me_3PO)_5](ClO_4)_2$	409

TABLE 28

Infrared Spectra of Five-coordinate Complexes (cm^{-1})[a]

Compound	ν(As-O)	ν(M-O)	Other Bands (500 - 200cm^{-1})
Me_3AsO	870s	-	266m
$[Mn(Me_3AsO)_5](ClO_4)_2$	869s, 863s	366m	284m
$[Mn(Me_3AsO)_4(ClO_4)]ClO_4$	868s, 855sh	368m br	306w, 279m
$[Fe(Me_3AsO)_4(ClO_4)]ClO_4$	861s	402m br	307m, 283sh
$[Fe(Me_3AsO)_4(ClO_4)]BPh_4$	855s	415m br	468w[b], 300m, 279m
$[Co(Me_3AsO)_5](ClO_4)_2$	867s, 857sh	407m, 391m	285m
$[Ni(Me_3AsO)_5](ClO_4)_2$	866s	407m	290m
$[Ni(Me_3AsO)_5](BF_4)_2$	866s	407m	291m, 278sh
$[Ni(Me_3AsO)_5](NO_3)_2$	866s	408m	290m, 279sh
$[Ni(Me_3AsO)_4(ClO_4)]ClO_4$	866s	407m br	283m
$[Ni(Me_3AsO)_4(ClO_4)]BPh_4$	864s	410m br	468w[b], 293m, 280sh
$[Ni(Me_3AsO)_4(NO_3)]BPh_4$[c]	880s, 866s	395sh, 385m	468w[b], 448m[d], 323m, 280m
$[Cu(Me_3AsO)_4(ClO_4)]ClO_4$	854m, 833s[e]	470m	288m, 268sh

[a] As Nujol mulls

[b] BPh_4 band.

[c] Octahedral complex

[d] Possibly metal-nitrate stretching absorption

[e] Contains methyl rocking mode normally observed at 840cm^{-1}

assignments. The simplicity of the ligand spectrum enables additional bands in the 360 - 470 cm^{-1} region to be assigned as metal-ligand stretching vibrations (Table 28). Only one such band was usually observed, although three could be expected for square pyramidal $[M(Me_3AsO)_5]^{2+}$ complexes[60] and an identifiable perchlorate γ(M-O) absorption for the $[M(Me_3AsO)_4(ClO_4)]^+$ complexes might be anticipated. It can be seen that lower γ(M-O) values arise from the five-coordinate $[Co(Me_3AsO)_5](ClO_4)_2$ complex as compared with values from the four-coordinate tetrahedral $[Co(Me_3AsO)_4](ClO_4)_2$ complex (Table 8). Table 29 also lists the frequencies for the related trimethylphosphine oxide complexes[21,131] which show the same trends. Assuming the generality of this effect, it may be used to distinguish between four- and five-coordination as mentioned on p.81 for the zinc complex. For the $[Ni(Me_3AsO)_5](ClO_4)_2$ and $[Ni(Me_3AsO)_4(ClO_4)]ClO_4$ complexes the γ(M-O) absorptions occur at the same frequency (407 cm^{-1}) confirming that both complexes have the same coordination number. Similarly for the manganese complexes $[Mn(Me_3AsO)_5](ClO_4)_2$ and $[Mn(Me_3AsO)_4(ClO_4)]ClO_4$ the γ(M-O) frequencies are at 366 and 368 cm^{-1} respectively.

The high ν(M-O) frequency (470 cm^{-1}) for the $[Cu(Me_3AsO)_4(ClO_4)]ClO_4$ complex may indicate a strengthening of the copper-trimethylarsine oxide M-O bond resulting from a weakening of the copper-perchlorate M-O bond (see Figure 9c). Such a distortion from the basic square pyramidal structure towards a square planar configuration could account for the slight differences between the X-ray powder photographs of the copper complex as compared with those of the other $[M(Me_3AsO)_4(ClO_4)]ClO_4$ (M = Mn, Fe and Ni) complexes. High ν(M-O) values appear to be typical of $[CuL_4(ClO_4)]ClO_4$ (L = Ph_3AsO, Ph_2MeAsO, Me_3PO) complexes[122]. In the Ph_2MeAsO series additional evidence for weak perchlorate association in the copper complex is obtained from the perchlorate absorptions. The $\nu_3(T_2)$ perchlorate band is split in the manganese, cobalt nickel and zinc complexes but not in the copper complex[121].

Solution Behaviour

All the complexes are decomposed in solution except $[Ni(Me_3AsO)_5](ClO_4)_2$ which is relatively stable in acetone. The manganese and iron complexes suffer immediate oxidation in nitromethane. The cobalt

complex $[Co(Me_3AsO)_5](ClO_4)_2$, when dissolved in nitromethane or acetone reverts to the blue tetrahedral $[Co(Me_3AsO)_4](ClO_4)_2$ derivative. The $[M(Me_3AsO)_4(ClO_4)]ClO_4$ (M = Ni and Cu) complexes are completely dissociated in solution, behaving as 1:2 electrolytes for M = Ni, Λ_m = 177 (nitromethane), 214 (acetone) for M = Cu, Λ_m = 179 ohm^{-1} $mole^{-1}$ cm^2. (nitromethane)) $[Ni(Me_3AsO)_5](ClO_4)_2$ appears to be more resistant to decomposition. The absorption spectrum in acetone, although showing some deviation from Beer's law, is essentially the same as that of the solid. The spectrum is unaffected by the addition of excess ligand. The compound is a 1:2 electrolyte in this solvent (Λ_m = 226 ohm^{-1} $mole^{-1}$ cm^2.) In nitromethane the compound shows spectral changes probably associated with partial dissociation, which can be prevented by the addition of excess ligand.

The octahedral $[Ni(Me_3AsO)_4(NO_3)]BPh_4$ complex is stable in nitromethane solution and behaves as a 1:1 electrolyte (Λ_m = 89 ohm^{-1} $mole^{-1}$ cm^2).

Comparison With Related Complexes

From the wide range of complexes with oxo-ligands now available, it appears that the $[M(Me_3AsO)_5]^{2+}$ (where M = Mn, Co and Ni) are the first examples of

five-fold coordination with identical oxo-ligands. Trimethylphosphine oxide forms analogous $[M(Me_3PO)_5]^{2+}$ complexes which have been studied by Miss S.H. Hunter [21,131] and it appears from a preliminary examination[21] that diphenylmethylphosphine oxide $[M(Ph_2MePO)_5]^{2+}$ complexes (where M = Fe, Co, Ni and Zn) can also be isolated. Although complexes of composition $Zn(Me_2SO)_5(ClO_4)_2$[132] and $Cd(Me_2SO)_5(ClO_4)_2$[133] have been reported, no evidence for five-coordination beyond the elemental analysis is presented. The trimethylphosphine and arsine oxides are apparently sufficiently small to enable five-fold coordination, but bulky enough to prevent six-coordination as found for other smaller oxo-ligands, such as pyridine N-oxide[134] and dimethylsulphoxide[135]. This is further indicated by the fact that the spectrum of the $[Ni(Me_3AsO)_5](ClO_4)_2$ complex is unaffected by excess ligand.

The $[M(Me_3AsO)_4(ClO_4)]ClO_4$ (M = Mn, Fe, Ni and Cu) complexes may be added to the number of complexes of composition type $ML_4(ClO_4)_2$, which are now known to be five-coordinate. It may be recalled that the cobalt and zinc trimethylarsine oxide $ML_4(ClO_4)_2$ complexes have a four-coordinate tetrahedral structure. Table 30 lists the five-coordinate $[ML_4(ClO_4)]ClO_4$

oxo-ligand complexes. There is evidence that all the copper complexes are distorted towards a square planar configuration (p.93).

It is interesting to consider the tendencies of the five-coordinate complexes to exhibit coordination numbers other than five. $[M(Me_3AsO)_6]^{2+}$ complexes could not be obtained but in association with a small bidentate ligand an octahedral complex $[Ni(Me_3AsO)_4(NO_3)]BPh_4$ can be isolated. In contrast the tetrahedral perchlorate ion acts only as a monodentate ligand in the $[M(Me_3AsO)_4(ClO_4)]^+$ complexes. While $[Ni(Me_3AsO)_5](ClO_4)_2$ is relatively stable in acetone, $[Co(Me_3AsO)_5](ClO_4)_2$ dissociates to the tetrahedral $[Co(Me_3AsO)_4](ClO_4)_2$ compound. With the polyamine Et_3dien, however, it is the five-coordinate cobalt complex that appears to be more stable. In acetone both $Co(Et_4dien)Cl_2$ and $Ni(Et_4dien)Cl_2$ are five-coordinate but in the solid state the nickel complex is square planar[120,124]. Such differences in behaviour appear to be related to the possible derived species.

In view of its similar shape to trimethylphosphine and arsine oxides, trimethylamine oxide might also be expected to form five-coordinate complexes. In this

work attempts to isolate such complexes gave only the previously reported four-coordinate complexes[136]. The ability of the amine oxide to form six-coordinate complexes, indicates that an $[M(Me_3NO)_5]$ species may not be stabilised by steric interactions as is postulated for the arsine oxide ligand. The addition of excess ligand to $[Co(Me_3NO)_4]^{2+}$ and $[Ni(Me_3NO)_4]^{2+}$ in nitromethane, produces spectral changes indicative of higher coordination, but complexes could not be isolated from these solutions. Similarly, it was not possible to isolate five-coordinate complexes using hexamethylphosphoramide, $(Me_2N)_3PO$, which like Me_3NO produces both four- and six-coordinate complexes[22,137].

The related thio-ligand, trimethylarsine sulphide, shows no tendency to give $[ML_5]^{2+}$ complexes. The spectra of the tetrahedral $[Co(Me_3AsS)_4]^{2+}$ and $[Ni(Me_3AsS)_4]^{2+}$ species in nitromethane are unaffected by the addition of excess ligand. This may be related to steric factors or the larger polarizability of the sulphur, and presumably more covalency, which are considered to favour a tetrahedral structure[102,103]. Six sulphur atoms can be accommodated around the nickel(II) ion as in $[Ni(etu)_6](ClO_4)_2$ but in the

absence of solid state effects the complex dissociates. In acetone solution, for example, an equilibrium between a square planar and an octahedral species occurs[47].

$$[Ni(etu)_6]^{2+} \rightleftharpoons [Ni(etu)_4]^{2+} + 2etu$$

TABLE 30

Five-Coordinate $[ML_4(ClO_4)]ClO_4$ Complexes

Ligand	Metal	Ref.
Me_3PO [a]	Fe, Cu	131
Me_3AsO [a]	Mn, Fe, Cu, Ni	c
Ph_2MePO	Mn, Fe, Co, Ni, Cu, Zn	122
Ph_2MeAsO	Mn, Fe, Co, Ni, Cu, Zn	121
Ph_3PO [b]	Mn, Fe, Co, Ni, Cu	122
Ph_3AsO [b]	Mn, Fe, Co, Ni, Cu	122

[a] For M = Co, Zn only tetrahedral $[ML_4](ClO_4)_2$ complexes have been isolated.

[b] For M = Co a tetrahedral complex can also be isolated, for M = Zn only a tetrahedral complex has been isolated.

[c] This work.

CHAPTER 4

EXPERIMENTAL

PREPARATION OF COMPLEXES

Generally the complexes were obtained by direct combination of stoichiometric ratios of the ligand and metal salt in hot anhydrous ethanol or acetone. The products, which separated on cooling, were washed with the solvent followed by dry ether, and dried under high vacuum. Where necessary, metal salts were dehydrated using ethylorthoformate[144]. Infrared spectra of the complexes were examined routinely to confirm the absence of water. Hygroscopic compounds were handled in a dry box.

Metal perchlorates were prepared from the action of perchloric acid on the metal carbonate. Similarly nickel fluoroborate was obtained from fluoroboric acid. Ferrous halides were freshly prepared from iron filings and the appropriate acid. The remaining halides were reagent grade samples. Thiocyanates were obtained by precipitating barium sulphate from aqueous solutions of barium thiocyanate and the metal sulphate.

1. Trimethylarsine Oxide Complexes

Perchloratotetrakis(trimethylarsine oxide)manganese(II) Perchlorate

Manganese perchlorate (0.16g) and trimethylarsine

oxide (0.24g.) reacted in ethanol under nitrogen to give a white complex, which is rapidly oxidised in air and in nitromethane solution. Found: C, 18.2; H, 4.6. $C_{12}H_{36}As_4Cl_2MnO_{12}$ requires C, 18.1; H, 4.5%.

Pentakis(trimethylarsine oxide)manganese(II) Perchlorate

Manganese perchlorate (0.21g.)and the ligand (0.40g.) yielded white crystals, from acetone containing ethylorthoformate. The complex, though reasonably stable in air, is rapidly oxidised in nitromethane. Found: C, 19.3; H, 4.8. $C_{15}H_{45}As_5Cl_2MnO_{13}$ requires C, 19.3; H, 4.8%.

Perchloratotetrakis(trimethylarsine oxide)iron(II) Perchlorate

A pale buff complex was obtained from ferrous perchlorate (0.25g.) and the oxide (0.38g.) in ethanol under nitrogen. The use of excess ligand or different solvents and temperatures gave the same complex. Although not oxidised in air, this complex decomposes immediately in nitromethane. Found: C, 17.5; H, 4.6; Fe, 7.3. $C_{12}H_{36}As_4Cl_2FeO_{12}$ requires C, 18.0; H, 4.5; Fe, 7.0%.

Perchloratotetrakis(trimethylarsine oxide)iron(II) Tetraphenylborate

This complex was prepared under nitrogen by adding ferrous perchlorate in ethanol to trimethylarsine oxide and sodium tetraphenylborate dissolved in the same solvent. The pale buff product which could not be obtained analytically pure has an infrared spectrum similar to the nickel analogue.

Dichlorobis(trimethylarsine oxide)iron(II)

Ferrous chloride (0.11g.) and the oxide (0.16g.) gave a pale buff powder from ethanol under nitrogen. The complex rapidly oxidises in air. Found: C, 17.8; H, 4.6; Cl, 17.3. $C_6H_{18}As_2Cl_2FeO_2$ requires C, 18.1; H, 4.5; Cl, 17.8%.

Dibromobis(trimethylarsine oxide)iron(II)

In the above preparation using ferrous bromide (0.10g.) and the ligand (0.13g.) a pale buff complex was precipitated. Similarly it decomposes rapdily in air. Found: C, 15.1; H, 3.7; Br, 32.6. $C_6H_{18}As_2Br_2FeO_2$ requires C, 14.8; H, 3.7; Br, 32.8%.

Pentakis(trimethylarsine oxide)cobalt(II) Perchlorate

Cobalt perchlorate (0.23g.) and trimethylarsine oxide (0.47g.) gave mauve crystals, from acetone containing ethylorthoformate. The complex is decomposed slowly by atmospheric moisture, turning a deep blue, and in nitromethane and acetone it decomposes to the tetrahedral $[Co(Me_3AsO)_4]^{2+}$ derivative. Found: C, 19.4; H, 4.9; Co, 5.9. $C_{15}H_{45}As_5Cl_2CoO_{13}$ requires C, 19.2; H, 4.8; Co, 6.3%.

Octahedral-dichlorobis(trimethylarsine oxide)cobalt(II)

This pale blue complex was obtained from ethanol solutions of cobalt chloride (0.36g.) and the ligand (0.45g.), or by recrystallising the tetrahedral form from the same solvent. The complex shows no tendency to revert to the tetrahedral form in the solid state and is insoluble in dichloromethane. Found: C, 17.9; H, 4.5; Cl, 17.9. $C_6H_{18}As_2Cl_2CoO_2$ requires C, 17.9; H, 4.5; Cl, 17.7%.

Octahedral-dibromobis(trimethylarsine oxide)cobalt(II)

A pale blue powder was precipitated by adding ether to the tetrahedral form dissolved in hot ethanol. Electronic reflectance spectra indicated that the complex

still contained a small amount of the tetrahedral impurity. The complex readily reverts completely to the tetrahedral form when dissolved in nitromethane, heated to 100°, exposed to atmospheric moisture or ground in the dry box. Found: C, 14.1; H, 3.6; Br, 32.7. $C_6H_{18}As_2Br_2CoS_2$ requires C, 14.65; H, 3.7; Br, 32.6%.

Pentakis(trimethylarsine oxide)nickel(II) Perchlorate

Nickel perchlorate (0.22g.) in acetone containing ethylorthoformate reacted with trimethylarsine oxide (0.42g.) in the same solvent to give hygroscopic orange crystals. Found: C, 19.15; H, 4.8; Ni, 6.3 $C_{15}H_{45}As_5Cl_2NiO_{13}$ requires C, 19.2; H, 4.8; Ni, 6.3%.

Pentakis(trimethylarsine oxide)nickel(II) Fluoroborate

In the above preparation using nickel fluoroborate (0.20g.) and the ligand (0.42g.) hygroscopic orange crystals were obtained. Found: C, 20.0; H, 5.4. $C_{15}H_{45}As_5B_2F_8NiO_5$ requires C, 19.2; H, 4.9%.

Pentakis(trimethylarsine oxide)nickel(II) Nitrate

Using nickel nitrate (0.11g.) and the oxide (0.24g.) the above preparation yielded very hygroscopic

orange crystals. Found: C, 20.5; H, 5.8. $C_{15}H_{45}As_5N_2NiO_{11}$ requires C, 20.9; H, 5.2%.

Perchloratotetrakis(trimethylarsine oxide)nickel(II) Perchlorate

Nickel perchlorate (0.20g.) and trimethylarsine oxide (0.28g.) reacted in ethanol containing ethylorthoformate to give a hygroscopic yellow powder. Found: C, 18.0; H, 4.6; Ni, 7.6. $C_{12}H_{36}As_4Cl_2NiO_{12}$ requires C, 18.0; H, 4.5; Ni, 7.3%.

Perchloratotetrakis(trimethylarsine oxide)nickel(II) Tetraphenylborate

Sodium tetraphenylborate (0.15g.) and the oxide (0.25g.) in ethanol were added to nickel perchlorate (0.17g.) in the same solvent with ethylorthoformate. A yellow product was precipitated. Found: C, 43.0; H, 5.6. $C_{36}H_{56}As_4BClNiO_8$ requires C, 42.3; H, 5.5%.

Nitratotetrakis(trimethylarsine oxide)nickel(II) Tetraphenylborate

In the above preparation using sodium tetraphenylborate (0.16g.), the ligand (0.25g.) and nickel nitrate (0.14g.) a yellow powder was obtained. Found:

C, 45.0; H, 5.8. $C_{36}H_{56}As_4BNNiO_7$ requires C, 43.9; H, 5.7%.

Dichlorobis(trimethylarsine oxide)nickel(II)

From ethanol solutions of nickel chloride (0.18g.) and trimethylarsine oxide (0.19g.) a pink complex was obtained. Traces of solvent in the product were removed by heating to 100° in vacuo. The complex is insoluble in nitromethane, dichloromethane, alcohol, acetone and dimethylformamide. Found: C, 18.3; H, 4.6; Cl, 17.7. $C_6H_{18}As_2Cl_2NiO_2$ requires C, 17.9; H, 4.5; Cl, 17.7%.

Dibromobis(trimethylarsine oxide)nickel(II)

A pink complex was obtained from the above preparation using nickel bromide (0.25g.) and the ligand (0.28g.). Similarly the complex is insoluble in the above solvents. Found: C, 14.4; H, 3.8; Br, 32.9. $C_6H_{18}As_2Br_2NiO_2$ requires C, 14.7; H, 3.7; Br, 32.6%. Attempts to prepare a tetrahedral form of the complex using different solvents or the method[79] used to produce the tetrahedral triphenylarsine oxide nickel(II) complexes were unsuccessful.

Dithiocyanatobis(trimethylarsine oxide)nickel(II)

A pale green product was prepared by mixing nickel thiocyanate (0.18g.) and trimethylarsine oxide (0.23g.) in ethanol containing ethylorthoformate. The complex, which is extremely hygroscopic, was recrystallised from anhydrous ethanol. Found: C, 20.9; H, 4.2; NCS, 25·6 . $C_8H_{18}As_2N_2NiO_2S_2$ requires C, 21.5; H, 4.0; NCS, 26.0%.

Dithiocyanatobis(trimethylphosphine oxide)nickel(II)

The above preparation yielded a pale green hygroscopic complex from nickel thiocyanate (0.15g.) and trimethylphosphine oxide (0.12g.). Found: C, 27.1; H, 5.4; NCS, 32·0 . $C_8H_{18}N_2NiO_2P_2S_2$ requires C, 26.8; H, 5.0; NCS, 32.4%.

Perchloratotetrakis(trimethylarsine oxide)copper(II) Perchlorate

Cupric perchlorate (0.19g.) and the oxide (0.29g.) gave a pale blue complex from ethanol. Found: C,17.9; H, 4.7. $C_{12}H_{36}As_4Cl_2CuO_{12}$ requires C, 17.9; H, 4.5%. Attempts to prepare a pentakis complex or a tetraphenylborate derivative were unsuccessful.

Tetrakis(trimethylarsine oxide)zinc(II) Perchlorate

Ethanol solutions of zinc perchlorate (0.18g.) and trimethylarsine oxide (0.27g.) reacted to give white crystals. Found: C, 17.6; H, 4.5. $C_{12}H_{36}As_4Cl_2O_{12}Zn$ requires C, 17.8; H, 4.5%. Attempts to prepare a five coordinate zinc complex using different solvents, temperatures and conditions of crystallisation were unsuccessful.

Dichlorobis(trimethylarsine oxide)zinc(II)

Zinc chloride (0.20g.) and the ligand (0.23g.) dissolved in acetone gave a white complex. Found: C, 17.8; H, 4.4; Cl, 17.1. $C_6H_{18}As_2Cl_2O_2Zn$ requires C, 17.7; H, 4.4; Cl, 17.4%.

Dibromobis(trimethylarsine oxide)zinc(II)

From ethanol solutions of zinc bromide (0.17g.) and the ligand (0.14g.) a white complex crystallised. Found: 14.6; H, 3.5; Br, 32.5. $C_6H_{18}As_2Br_2O_2Zn$ requires C, 14.5; H, 3.6; Br, 32.1%.

2. Trimethylarsine Sulphide Complexes

Tetrakis(trimethylarsine sulphide)iron(II) Perchlorate

Ferrous perchlorate (0.25g.) and trimethylarsine

sulphide (0.35g.) reacted in ethanol to give white crystals. Though stable in air the complex is rapidly oxidised in nitromethane solution. Found: C, 17.3; H, 4.4; Fe, 6.8; $C_{12}H_{36}As_4Cl_2FeO_8S_4$ requires C, 16.7; H, 4.2; Fe, 6.5%.

Dichlorobis(trimethylarsine sulphide)iron(II)

A pale buff powder was formed under nitrogen from ethanol solutions of ferrous chloride (0.24g.) and the sulphide (0.30g.). Oxidation of the complex in air is slow. Found: C, 16.8; H, 3.8; Cl, 16.0. $C_6H_{18}As_2Cl_2FeS_2$ requires C, 16.7; H, 4.2; Cl, 16.4%.

Dibromobis(trimethylarsine sulphide)iron(II)

In the above preparation pale buff crystals were obtained using ferrous bromide (0.35g.) and the ligand (0.33g.). The complex is reasonably stable in air but decomposes in dichloromethane and nitromethane solutions. Found: C, 13.8; H, 3.5; Br, 30.5. $C_6H_{18}As_2Br_2FeS_2$ requires C, 13.9; H, 3.5; Br, 30.7%.

Tetrakis(trimethylarsine sulphide)cobalt(II) Perchlorate

The complex was prepared as blue crystals from acetone solutions of cobalt perchlorate (0.37g.) and

trimethylarsine sulphide (0.60g.). Found: C, 16.8; H, 4.1; Co, 6.7. $C_{12}H_{36}As_4Cl_2CoO_8S_4$ requires C, 16.6; H, 4.2; Co, 6.8%.

Dichlorobis(trimethylarsine sulphide)cobalt(II)

Cobalt chloride (0.36g.) and trimethylarsine sulphide (0.42g.) reacted in ethanol to give deep blue crystals. Found: C, 16.9; H, 4.1; Cl, 15.9. $C_6H_{18}As_2Cl_2CoS_2$ requires C, 16.6; H, 4.2; Cl, 16.3%.

Dibromobis(trimethylarsine sulphide)cobalt(II)

Blue crystals were obtained from cobalt bromide (0.33g.) and the sulphide (0.30g.) dissolved in ethanol . Found: C, 14.2; H, 3.6; Br, 30.7. $C_6H_{18}As_2Br_2CoS_2$ requires C, 13.8; H, 3.4; Br, 30.6%.

Diiodobis(trimethylarsine sulphide)cobalt(II)

In the above preparation using cobalt iodide (0.35g.) and

the ligand (0.30g.) green crystals were obtained. Increasing the ligand:metal salt ratio did not change the product obtained. Found: C, 12.0; H, 3.3; I, 41.4. $C_6H_{18}As_2CoI_2S_2$ requires C, 11.7; H, 2.9; I, 41.1%.

Dithiocyanatobis(trimethylarsine sulphide)cobalt(II)

Deep blue crystals separated from ethanol solutions of cobalt thiocyanate (0.23g.) and trimethylarsine sulphide (0.30g.). Found: C, 19.8; H, 3.8; Co, 12.2. $C_8H_{18}As_2CoN_2S_2$ requires C, 20.0; H, 3.8; Co, 12.3%.

Tetrakis(trimethylarsine sulphide)nickel(II) Perchlorate

Nickel perchlorate (0.30g.) and the sulphide (0.40g.) gave green crystals from acetone. Found: C, 17.2; H, 4.5; Ni, 6.6. $C_{12}H_{36}As_4Cl_2NiO_8S_4$ requires C, 16.6; H, 4.2; Ni, 6.8%.

Dichloro(trimethylarsine sulphide)nickel(II)

Nickel chloride (0.42g.) and trimethylarsine sulphide (0.55g.) reacted in ethanol, containing ethyl orthoformate, to give a green solution from which a yellow solid separated. The complex, which was

recrystallised from alcohol-acetone solution, is rapidly hydrated in air. Found: C, 13.3; H, 3.2; Cl, 25.1. $C_3H_9AsCl_2NiS$ requires C, 12.8; H, 3.2; Cl, 25.2%.

Dichlorobis(trimethylarsine sulphide)nickel(II)

Nickel chloride (0.20g.) and excess ligand (0.67g.) were dissolved in ethanol and the hot solution rapidly evaporated in vacuo. Dark green hygroscopic crystals which separated out were washed with dry benzene. Found: C, 16.6; H, 4.0; Cl, 16.8. $C_6H_{18}As_2Cl_2NiS_2$ requires C, 16.6; H, 4.15; Cl, 16.3%.

Dibromobis(trimethylarsine sulphide)nickel(II)

This green complex crystallised from ethanol solutions of nickel bromide (0.27g.) and trimethylarsine sulphide (0.30g.). Found: C, 13.6; H, 3.4; Br, 30.5. $C_6H_{18}As_2Br_2NiS_2$ requires C, 13.8; H, 3.4; Br, 30.6%.

Tetrakis(trimethylarsine sulphide)zinc(II) Perchlorate

Zinc perchlorate (0.24g.) and the sulphide (0.35g.) gave white crystals from ethanol. Found: C, 16.9; H, 4.2. $C_{12}H_{36}As_4Cl_2O_8S_4Zn$ requires C, 16.5; H, 4.1%.

Dichlorobis(trimethylarsine sulphide)zinc(II)

Zinc chloride (0.15g.) and trimethylarsine sulphide (0.35g.) dissolved in ethanol gave a white complex. Found: C, 16.6; H, 4.2; Cl, 16.2. $C_6H_{18}As_2Br_2S_2Zn$ requires C, 16.4; H, 4.1; Cl, 16.1%.

Dibromobis(trimethylarsine sulphide)zinc(II)

In the above preparation using zinc bromide (0.23g.) and the ligand (0.30g.) a white product was obtained. Found, C, 14.0; H, 3.6; Br, 29.8. $C_6H_{18}As_2Br_2S_2Zn$ requires C, 13.6; H, 3.4; Br, 30.2%.

Trichloro(nitrosyl)bis(trimethylarsine sulphide)-ruthenium(III)

Hydrated $RuCl_3(NO)$ (0.27g.) and the sulphide (0.30g.) reacted in ethanol to give a red-brown powder. Found: C, 13.5; H, 3.3; $C_6H_{18}As_2Cl_3NORuS_2$ requires C, 13.3; H, 3.3%.

Reaction with Copper(II) Perchlorate

Copper perchlorate (0.14g.) and trimethylarsine sulphide (0.22g.) when mixed in ethanol immediately gave a white precipitate, whose infrared spectrum indicated that it contained coordinated trimethyl-

arsine sulphide. The complex was diamagnetic but did not analyse satisfactorily. This reaction was not investigated further.

3. Trimethylphosphine Sulphide Complexes

Tetrakis(trimethylphosphine sulphide)cobalt(II) Perchlorate

Cobalt perchlorate (0.37g.) and trimethylphosphine sulphide (0.48g.) reacted in ethanol containing ethyl orthoformate to give blue crystals. Found: C, 21.1; H, 5.1; Co, 8.3; $C_{12}H_{36}Cl_2O_8P_4S_4$ requires C, 20.9; H, 5.2; Co, 8.5%.

Dichlorobis(trimethylphosphine sulphide)cobalt(II)

In the above preparation using cobalt chloride (0.30g.) and the ligand (0.30g.) a blue complex was obtained. Found: C, 20.9; H, 5.2; Cl, 20.0. $C_6H_{18}Cl_2CoP_2S_2$ requires C, 20.8; H, 5.2; Cl, 20.5%.

Dibromobis(trimethylphosphine sulphide)cobalt(II)

Reaction of cobalt bromide (0.41g.) and the sulphide (0.30g.) in ethanol containing ethyl orthoformate yielded a blue complex. Found: C, 16.7; H, 4.2; Br, 36.6; $C_6H_{18}Br_2CoP_2S_2$ requires C, 16.6;

H, 4.1; Br, 36.7%.

Diiodobis(trimethylphosphine sulphide)cobalt(II)

This green complex was prepared as above from cobalt iodide (0.51g.) and the sulphide (0.30g.).
Found: C, 13.9; H, 3.4; Co, 10.8.
$C_6H_{18}CoI_2P_2S_2$ requires C, 13.6; H, 3.4; Co, 11.1%.

4. Triphenylarsine Sulphide Complexes

Tetrakis(triphenylarsine sulphide)cobalt(II) Perchlorate

Rapid evaporation of a hot ethanol solution of cobalt perchlorate and triphenylarsine sulphide in the presence of ethylorthoformate gave a viscous product. A blue solid was obtained on cooling and adding ether, but it was contaminated with unreacted components. These could not be eliminated by recrystallisation, use of different solvents or different reactant ratios. The complex, which is decomposed by ethanol and acetone was identified as $[Co(Ph_3AsS)_4](ClO_4)_2$ from its isomorphism with the pure zinc analogue. Reaction of cobalt perchlorate and the sulphide ligand in tetrahydrofuran yielded a blue complex with an infrared spectrum typical of triphenylarsine oxide complexes.

Dibromobis(triphenylarsine sulphide)cobalt(II)

This complex was prepared as in the above preparation using cobalt bromide. Similarly an analytically pure product could not be obtained. Found: C, 46.4; H, 3.5. $C_{36}H_{30}As_2Br_2CoS_2$ requires C, 48.3; H, 3.35%.

Tetrakis(triphenylarsine sulphide)zinc(II) Perchlorate

Zinc perchlorate (0.21g.) and the ligand (0.40g.) in ethanol containing ethylorthoformate yielded a white complex. Found: C, 53.0; H, 3.9. $C_{72}H_{60}As_4Cl_2O_8S_4Zn$ requires C, 53.4; H, 3.7%.

PREPARATION OF LIGANDS

The ligands were synthesised from the parent phosphine or arsine by published methods[18,56].

1. Trimethylarsine

This was prepared from arsenic trichloride (1 mole) and a Grignard reagent[138] (3 moles). All glassware was preheated and flushed with dry nitrogen. The reaction was carried out in a 3 litre flask fitted with a double surface condenser, a nitrogen inlet and a dropping funnel. Methyl iodide (190 ml) in dry di-n-butyl ether (200 ml) was added dropwise to magnesium (73g.) in the same solvent (1 l). The reaction was initiated by adding iodine and heating to 50°. The temperature was kept between 50 - 70° using an ice-bath. On completion of the Grignard, the condenser was replaced by a stirrer and the reaction mixture cooled to 0°. Arsenic trichloride (80 ml) in di-n-butyl ether (100 ml) was then added dropwise over a period of 2 hours. Efficient stirring was needed to prevent solidification of the reaction mixture. The stirring was continued at room temperatures for an hour, after which the stirrer and dropping funnel were removed and a fractionating column fitted. The temperature of the

reaction was gradually raised, using an oil bath, to 160°. The arsine distilled off (~ 70°) into a graduated dropping funnel. The trimethylarsine was stored as a silver iodide adduct[139]. This is most easily prepared by shaking the arsine with an aqueous silver iodide-potassium iodide solution. Decomposition of the adduct is carried out by heating to 160° in vacuo.

2. Trimethylarsine Oxide

130 volume hydrogen peroxide (13 ml) in acetone (20 ml) was added dropwise to trimethylarsine (15 ml) in deoxygenated acetone (60 ml) under nitrogen. The reaction was cooled using an ice-bath . The solution was then refluxed gently for an hour and evaporated on a water bath until crystallisation began. The crude product was placed in a vacuum desiccator over concentrated sulphuric acid to complete crystallisation and finally purified by sublimation under high vacuum at 120 - 150°. Since trimethylarsine oxide is extremely hygroscopic it was always handled in a dry box.
Melting point: 193 - 195° (lit. value[18]: 191.2 - 195.2°).

3. Trimethylarsine Sulphide

Trimethylarsine (20 ml) and sulphur (6g.) were

refluxed in dry ethanol (200 ml) for an hour under nitrogen. Excess sulphur was filtered off and on cooling the product crystallised. Trimethylarsine sulphide was recrystallised twice from ethanol. Melting point: 184 - 185° (lit. value[140]: 183 - 184°).

4. Trimethylphosphine

Trimethylphosphine was prepared by Mr R.C. Rendle in a manner similar to that used for the arsine[138,141]. It was also stored as a silver iodide adduct[139] which can be decomposed by heating to 160° in vacuo[142].

5. Trimethylphosphine Sulphide

Trimethylphosphine (10ml) and sulphur (5g) were refluxed in dry ether (200 ml) for 10 hours under nitrogen. The remaining sulphur was filtered off and the solution evaporated to dryness. The crude product was twice recrystallised from warm ethanol, solutions being concentrated in a vacuum desiccator over concentrated sulphuric acid. Melting point: 155 - 156° (lit. value[54]: 155.5 - 156°).

6. Triphenylarsine Sulphide

Triphenylarsine (7.5g.) and sulphur (0.8g.) were heated at 170° in a sealed tube under nitrogen for

two hours. The product was recrystallized from ethanol. Melting point: 163°, (lit. value[143]: 163.5°).

PHYSICAL METHODS, ANALYSES, AND REAGENTS

1. Infrared Spectra

Infrared spectra were recorded using Perkin-Elmer 337 (to 400 cm^{-1}) and Grubb Parsons DM4 (500 - 200 cm^{-1}) spectrophotometers. Calibrations were made with polystyrene and water vapour respectively. Solid samples were run on nujol or hexachlorobutadiene (nitrates only) mulls, using KBr plates (to 400 cm^{-1}) and polythene discs or CsI plates (500 - 200 cm^{-1}). Moisture sensitive samples were mulled and placed between the plates in a dry box. For solution spectra (500 - 200 cm^{-1}), the complexes were dissolved in nitromethane and placed in 0.2mm polythene cells. Nitromethane is free of absorptions between 450 and 200 cm^{-1}.

2. Electronic Spectra

Electronic spectra were recorded using a Beckman DK 2A spectrophotometer. For solid samples, the Beckman reflectance attachment was used and the spectra run against magnesium oxide as standard. Where necessary, the sample was diluted with magnesium oxide. For solution spectra, the complexes were

dissolved in dichloromethane, nitromethane or acetone and placed in 1 cm cells. The molar extinction coefficients, ϵ, were determined from the expression

$$\epsilon = D/(c \times d)$$

where D is the optical density

c the concentration (mole litre^{-1})

and d the path length (cm)

The oscillator strengths, f, were evaluated graphically using the expression[145]

$$f = 4.32 \times 10^{-9} \int \epsilon \, d\nu$$

where ν is the frequency in cm^{-1}.

3. Magnetic Measurements

Magnetic susceptibilities were determined by the Gouy method[146] using $Ni(en)_3S_2O_3$[147] as calibrant. Reproducibility of the magnetic moments is $\pm$ 0.04 B.M.

The magnetic moment, μ, was calculated from the expression

$$\mu = 2.84(\chi_m^{corr} \times T)^{\frac{1}{2}}$$

where T is the absolute temperature and χ_m^{corr} the molar susceptibility corrected for diamagnetism using Pascal constants[146]. The diamagnetic susceptibility of trimethylarsine sulphide was measured as -0.104×10^{-3} as compared with the calculated value of -0.102×10^{-3}

cgsu. For the tetrahedral cobalt(II) complexes, corrections were also made for temperature independent paramagnetism using the expression $2.09/\Delta$.[36]

For $[Co(Me_3AsS)_4](ClO_4)_2$, the reciprocal of χ_m^{corr} was plotted against T (195, 260 and 273°K), and from the resulting straight line, the value of θ was obtained.

4. X-ray Powder Photographs

X-ray powder photographs were obtained using a Philips 114.83mm camera with CuK_α radiation. Finely ground samples were packed into Lindemann tubes.

5. Conductivity Measurements

Conductivity measurements were made at 25°C using a Philips PR9550/01 bridge and a cell with removable dip-type platinum electrodes. The cell was calibrated with a standard potassium chloride solution[148].

The molar conductivity, Λ_m, is given by

$$\Lambda_m = \frac{1000K}{C}$$

where K is the specific conductivity and C the concentration (mole litre^{-1}). The specific conductivity, K, is given by

$$K = \frac{\text{cell const.}}{R}$$

where R is the resistance of the solution (ohm). Representative values of Λ_m for solvents used in this section are:

Ion type	Nitrobenzene	Nitromethane	Acetone
1:1	20-30	70-90	100-130
1:2	45-55	150-170	230-250
1:3	70-80	230-250	350-370

6. Analyses

The complexes were decomposed in aqueous solution. The analytical proceedures used are described by Vogel[149]. Halide was determined by the Volhard titration and the metals were determined gravimetrically (Iron as Fe_2O_3, cobalt as $Co(py)_4(SCN)_2$ and nickel as the dimethylgloximate). Carbon and hydrogen analyses were carried out at the Micro-analytical Laboratory, University of Otago.

7. Drying and Purification of Solvents

Acetone (A.R. grade) was dried over potassium carbonate.

Di-n-butyl Ether was washed with a ferrous sulphate solution[150], followed by water and dried over calcium

chloride. It was then fractionally distilled (B.Pt 140 - 142°) and stored over sodium.

Dichloromethane was dried over magnesium sulphate, fractionally distilled (B.Pt 39 - 40°) and stored over molecular sieves.

Diethyl Ether was dried over sodium.

Ethanol was dried using magnesium activated with iodine[150]. 0.5g. iodine and 5g. magnesium were added to 50 - 75cc of absolute alcohol and warmed until the iodine colour disappeared. When all the magnesium was converted to the ethylate 900cc of absolute alcohol were added and refluxed for one hour. The alcohol was distilled off and stored over molecular sieves.

Nitrobenzene (AR grade) and nitromethane were dried over molecular sieves.

8. Dehydrating Agent

Ethylorthoformate[144] has been used extensively in this section as a rapid dehydrating agent. Dehydration of hydrated metal salts is conveniently carried out in the reaction mixture. The reagent reacts with water in the presence of acid catalysts as follows

$$(C_2H_5O)_3CH + H_2O \rightarrow 2C_2H_5OH + C_2H_5OOCH.$$

APPENDICES

APPENDIX I

In the course of the comparative study of oxo- and thio-ligand complexes, several systems were investigated but found to be impracticable. The systems, which involved ligands of the type Ph_3ZY (where Z = P and As; Y = O and S), will be described briefly.

1. Dichlorodicarbonylruthenium(II)

The action of carbon monoxide on an ethanol (or 2-methoxy ethanol) solution of hydrated ruthenium trichloride gives a deep red (or yellow) solution, from which a series of $RuCl_2(CO)_2L_2$ (L = amine, phosphine, arsine or stibine) complexes can be isolated[151,152]. In the present work attempts to prepare Ph_3ZY complexes from the ethanol solution were unsuccessful. From 2-methoxy ethanol, however, $RuCl_2(CO)_2(Ph_3PO)_2$ was prepared. The observation of two ν(C-O) bands in the infrared indicates a cis arrangement of the carbonyl ligands[152]. The reaction of triphenylphosphine sulphide with the 2-methyl ethanol solution gave a product with four ν(C-O) bands in the infrared. A band at 637 cm^{-1}, attributable to ν(P-S) in the uncomplexed ligand, was also observed. Repeated recrystallisation did not improve the purity

of the product. With triphenylarsine oxide and sulphide, reduction of the ligand occurred, the products showing identical infrared spectra (4000 - 400 cm^{-1}), typical of triphenylarsine complexes. The observation of ν(C-O) at 2063, 2004 cm^{-1} indicates the products are probably cis-$RuCl_2(CO)_2(Ph_3As)_2$ [152].

Experimental

Carbon monoxide was passed into a refluxing 2-methoxy ethanol solution (50 ml) of hydrated ruthenium trichloride (2g.) for 4 hours.

Dichlorobis(carbonyl)bis(triphenylphosphine oxide) ruthenium(II)

To the above yellow solution (12 ml), triphenylphosphine oxide (1.07 g.) was added and the solution refluxed for 3 hours. The pale yellow product was recrystallised from a dichloromethane ethanol mixture. The infrared spectrum showed bands at 2054, 1973 (C-O) and 1159 cm^{-1} (P=O). Found: C, 57.3; H, 4.2. $C_{38}H_{30}Cl_2O_4P_2Ru$ requires C, 58.2; H, 3.8%.

2. Ruthenium(III)

Dark brown or green powders were formed from ethanol solutions of ruthenium trichloride and the

Ph_3ZY ligands. Infrared spectra indicated the presence of coordinated ligand, but analyses showed that less than one mole of ligand was coordinated per mole of ruthenium trichloride. Refluxing with excess ligand did not significantly increase this ratio.

3. Platinum(II)

Neither Ph_3PO nor Ph_3AsO reacted with Zeise's salt, although the pyridine N-oxide complex $[PtCl_2(C_2H_4)(pyO)]$ is known[153].

APPENDIX II

CALCULATION OF SPECTROCHEMICAL PARAMETERS (Δ AND β)

1. Tetrahedral Cobalt(II)

The Tanabe-Sugano matrices for tetrahedral cobalt(II) are[38]

$$^4A_2(F) \quad : \quad -12Dq - 15B$$

$$^4T_2(F) \quad : \quad -2Dq - 15B$$

$$^4T_1(F),\ ^4T_1(P) \quad : \quad \begin{vmatrix} -2Dq - 3B & 6B \\ 6B & 8Dq - 12B \end{vmatrix}$$

The transitions $^4A_2(F) \longrightarrow {}^4T_2(F)$, $^4A_2(F) \longrightarrow {}^4T_1(F)$, and $^4A_2(F) \longrightarrow {}^4T_1(P)$ are designated as ν_1, ν_2 and ν_3 respectively. The lowest energy transition, ν_1, is found as

$$\nu_1 = E(^3T_2) - E(^4A_2) = 10Dq \qquad (1)$$

and should give 10Dq directly, but the band is not often observed[38]. The separation between the $^4A_2(F)$ and $^4T_1$ states is found by evaluating the determinant of the matrix. The eigenvalues, E, are

$$E = 3Dq - 7.5B \pm Q$$

where $Q = \frac{1}{2}[(-6Dq + 15B)^2 + 64(Dq)^2]^{\frac{1}{2}}$

Hence $\nu_2 = E(^4T_1(F)) - E(^4A_2)$

$= 15Dq + 7.5B - Q \qquad (2)$

and $\nu_3 = E(^4T_1(P)) - E(^4A_2)$

$= 15Dq + 7.5B + Q \qquad (3)$

From equations (2) and (3), and substituting Δ for 10Dq

$\Delta = [7.2(\nu_2 + \nu_3) - (51.84(\nu_2+\nu_3)^2 - 217.6\,\nu_2\nu_3)^{\frac{1}{2}}]/27.2$

$B = [\nu_2 + \nu_3 - 3\Delta]/15$

B is usually lower in the complex than in the free ion, and is referred to as B'

$\beta = B'/B(\text{free ion})$

Assignment of the ν_2 and ν_3 bands therefore allows the evaluation of Δ and β.

2. Tetrahedral Nickel(II)

Since the effects of spin-orbit coupling are more important for tetrahedral nickel(II) than for tetrahedral cobalt(II), it has been found that use of

the Tanabe-Sugano matrices, which do not include spin-orbit coupling, yields unlikely Δ values[92]. Therefore in the present work, the complete theory of Liehr and Ballhausen[94], which includes the spin-orbit coupling parameter, λ, has been used.

The determinants, which involve the parameters F_2, F_4, λ and Dq, are given on pages 140 - 141 of Liehr and Ballhausen's paper[94]. The Stater-Condon parameters, F_2 and F_4, are related to the Racah B parameter by[145]

$$B = F_2 - 5F_4.$$

Assuming[92,94]

$$F_2 = 14F_4$$

the determinants were expressed in terms of the parameters B, λ and Dq only. The parameters were then varied, using a computer programme written by R.S. Anderson and I.N. Douglas (Physics Department, University of Canterbury) until the best fit between the calculated and observed spectrum (see Table 19) was obtained.

4. Octahedral Cobalt(II)

The Tanabe-Sugano matrices for octahedral cobalt(II) in a weak field are[72]

$^4T_{1g}(F)$, $^4T_{1g}(P)$: $\begin{vmatrix} -6Dq & 4Dq \\ 4Dq & B \end{vmatrix}$

$^4T_{2g}(F)$: 2Dq

$^4A_{2g}(F)$: 12Dq

The transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ are designated ν_1, ν_2 and ν_3 respectively. Since the ν_2 transition corresponds to a two-electron transition, the absorption band should be weak[72], and may not be observed. Values of the parameters, Δ and β, can therefore be obtained from the positions of the ν_1 and ν_3 bands.

The eigenvalues, E, of the determinant are

$$E = -3Dq + 7.5B \pm Q$$

where

$$Q = \tfrac{1}{2}[(6Dq + 15B)^2 + 64(Dq)^2]^{\frac{1}{2}}$$

Hence $\nu_1 = E(^4T_{2g}) - E(^4T_{1g}(F))$

$$= 5Dq - 7.5B + Q \qquad (1)$$

$\nu_3 = E(^4T_{1g}(P)) - E(^4T_{1g}(F))$

$$= 2Q \qquad (2)$$

From equations (1) and (2), and substituting Δ for 10Dq

$$\Delta = [(2\nu_1 - \nu_3)^2 + (\nu_3^2 + \nu_1\nu_3 - \nu_1^2)^{\frac{1}{2}}]/2$$

$$B = [\nu_3 - 2\nu_1 + \Delta]/15$$

Assignment of the ν_1 and ν_3 bands therefore allows the evaluation of Δ and β. The position of ν_2 can be calculated

$$\nu_2 = E(^4A_{2g}) - E(^4T_{1g}(F))$$

$$= 15Dq - 7.5B + Q \qquad (3)$$

From equations (1) and (3) and substituting Δ for 10Dq

$$\nu_2 = \Delta + \nu_1$$

A similar expression for Δ given by Eilbeck, Holmes and Underhill[154] contains an error.

4. Octahedral Nickel(II)

For octahedral nickel(II) the transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ are designated as ν_1, ν_2 and ν_3 respectively. The lowest energy transition, ν_1, gives Δ (or 10Dq) directly and B is calculated from the expression[155]

$$B = [\nu_2 + \nu_3 - 3\Delta]/15$$

SECTION II

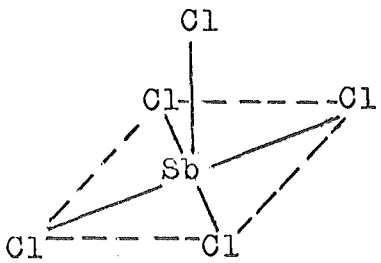
SOME COMPLEXES OF THE GROUP VB TRIHALIDES

INTRODUCTION

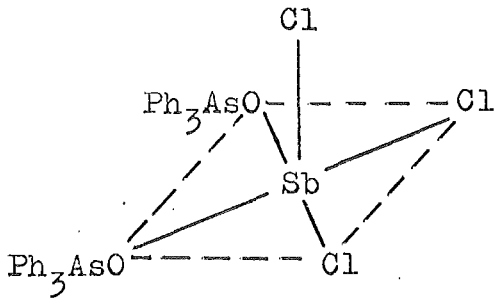
Group VB complexes are predominantly of the type $MX_3 2L'$, $MX_3 L''$ and MX_5^{2-} (where M = As, Sb and Bi; X = Cl, Br and I; L' = monodentate and L'' = bidentate ligand). However, 1:1 adducts are known and the complex halide anions cover a wide range of compositions.

Since no structure determinations have been made on simple arsenic trihalide adducts it is not known if their stereochemistry is influenced by the lone pair of electrons. $Cs_3As_2Cl_9$ appears to contain, not $[As_2Cl_9]^{3-}$ units but pyramidal $AsCl_3$ molecules surrounded by Cs^+ and Cl^- ions[156]. In a number of antimony(III) compounds the coordination is square pyramidal, presumably due to the stereochemically active lone pair. For example K_2SbF_5[157], $(NH_4)_2SbCl_5$[158], and $SbCl_3 2Ph_3AsO$[159] exhibit this stereochemistry (Figure 1). In $SbCl_3 2Ph_3AsO$ the ligands occupy cis basal positions. Even when the stoichiometry does not demand it, five-coordination is achieved in $KSbF_4$ and $NaSbF_4$. These contain $[Sb_4F_{16}]^{4-}$ units with cis fluorine bridges and antimony in a square pyramidal environment[155]. The influence of the lone pair is again apparent in $Bi_{12}Cl_{14}$ which consists of square pyramidal $[BiCl_5]^{2-}$

FIGURE 1. Structures of $(NH_4)_2SbCl_5$ and $SbCl_3 2Ph_3AsO$.



a. $SbCl_5^{2-}$ anion.



b. $SbCl_3 2Ph_3AsO$

units and pairs of such units sharing a basal edge, as well as Bi_9^{5+} clusters[160]. The slight displacement of the metal atom below the basal plane in these complexes has been attributed to repulsions between the nonbonding and bonding pairs of electrons[161].

In the anion of the pyridinium salt $(C_5H_5NH)(SbCl_4)$, an infinite chain structure is found with cis chlorine bridges and antimony in an octahedral environment[162]. Similar structures have been reported for the anions, SbI_4^-, $BiBr_4^-$, and BiI_4^-, in their 2-picolinium salts[163]. Structurally, the $BiBr_5^{2-}$ anion, in its piperidinium salt, consists of a distorted octahedral arrangement of bromines about the bismuth, with two cis bromines linking adjacent bismuth atoms[164]. The analogous $SbBr_5^{2-}$ is reported to be isomorphous[164]. Discrete octahedral units are found in $(Me_2NH_2)_3(BiBr_6)$[165]. There is little evidence for the lone pair being stereochemically active in these six-coordinate complexes, which generally involve the heavier halogens.

Little is known about the relative stabilities of the various complex halide anions of the Group VB trihalides, apart from the apparent increase in such complexes on going down the group[157]. The higher anions are restricted to the heavier elements, simple

AsX_6^{3-} anions being unknown. Recent systematic studies on the reaction of amine hydrohalides with antimony trihalides yielded mainly salts with an Sb:X ratio of 1:5[166-168]. However, it was found that no such complexes were formed from similar reactions with bismuth triiodide, the predominant Bi:I ratio being 2:9[169].

Nitrogen donor ligands react readily with the trihalides of arsenic, antimony and bismuth. With 2,2'-dipyridyl, a series of nine MX_3dipy complexes is known. Ionization trends of these complexes in nitrobenzene suggest an increasing preference for higher coordination numbers down the group[170]. Monodentate nitrogen ligands react with the trihalides with a diversity of combining ratios. $AsCl_3NMe_3$, $SbCl_3NMe_3$ and $(SbCl_3)_2NEt_3$ have been prepared[171], and pyridine complexes vary (Table 1). Table 1 suggests the importance of bis-pyridine adducts, but in some cases analytical data are unsatisfactory.

Oxo-ligands show a more definite preference for the formation of 1:2 complexes with the Group VB trihalides. Triphenylphosphine oxide gives complexes of the type $MX_3 2Ph_3PO$ with $AsCl_3$, $SbCl_3$ and BiX_3 (X = Cl, Br, I)[179], and $POCl_3$[180], Me_3PO[181], Ph_3AsO[32] and

TABLE 1

Reported Group VB Trihalide Pyridine Complexes[a]

$AsCl_3py$	$AsBr_3 2py$[b]	$AsI_3 2py$
$AsCl_3 2py$	$AsBr_3 3py$[c]	$AsI_3 3py$
$SbCl_3py$[d]	$4SbBr_3 7py$	$2SbI_3 3py$
$2SbCl_3 3py$[e]		
$SbCl_3 2py$[f]		
$BiCl_3 2py$	$BiBr_3 2py$	

[a] From refs 172-178

[b] M.Pt. 195° (ref. 175)

[c] M.Pt. 194° (ref. 174)

[d] M.Pt. 184° (refs. 174,177), 164° (ref. 176).

[e] M.Pt. 185° (ref. 176).

[f] M.Pt. 185° (ref. 178).

Me_2SO[180] all give $SbCl_3 2L$ complexes. $BiCl_3 2POCl_3$[182] has also been reported. A number of 1:1 adducts are also known[159].

Several VB halide complexes with phosphines[171], arsines[183] and sulphides[184] have been reported, but since the present work is concerned with oxygen and nitrogen donor ligands, these will not be mentioned further.

A general consideration of Group trends for the trihalides of phosphorus, arsenic, antimony, and bismuth indicate that the complexes of the heavier elements are more stable and greater in number. Phosphorus trihalides only form weak and easily dissociable adducts, while antimony and bismuth show an increasing tolerance for higher coordination numbers[157].

In the present work the low frequency infrared spectra of a selection of addition compounds formed between oxygen and nitrogen donor ligands has been studied. The first objective was to prepare a series of $MX_3 2L'$ and $MX_3 L''$ (L' = mono-, L'' = bidentate ligand) adducts. 2,2'-Dipyridyl readily gives a series of nine such complexes[170] thus facilitating a low frequency infrared study. For comparison with the dipyridyl series, several pyridine adducts were studied. The

steric requirements of 2,2',2"-terpyridyl tend to emphasise any coordination preferences of the acceptor molecule. It was therefore chosen because of its chemical rather than infrared interest. To confirm the assignments of metal-ligand and metal-halogen vibrations, the spectra of triphenylarsine oxide and pyridine N-oxide complexes were examined. Since the structure of $SbCl_3.2Ph_3AsO$ is known[159], it served as a reference five-coordinate compound. The assignment of the metal-ligand stretching frequencies for these complexes prompted an examination and assignment of the spectra of some related Group IVB halide adducts.

RESULTS AND DISCUSSION

In most cases the Group VB trihalides reacted to give $MX_3 2L'$ or $MX_3 L''$ complexes, although there were some exceptions. The compounds, including many characterized for the first time, were prepared by reacting the ligands directly with the trihalide in an inert solvent, under anhydrous conditions. Many of the adducts, especially those of arsenic, are extremely sensitive to hydrolysis by atmospheric moisture and so as a precaution all complexes were handled in a dry box. The low solubilities of the complexes prevented the measurement of their molecular weights; however, most dissolved sufficiently in nitrobenzene for molar conductivity measurements.

Pyridine Complexes

Previously reported pyridine complexes are listed in Table 1. In the present work, an attempt to prepare bis complexes was made by reacting excess pyridine with the appropriate trihalide. Such complexes were formed with the tribromides of arsenic, antimony and bismuth. The melting point found for $AsBr_3 2py$ (195^{o}) agrees with Dafert and Melinski[175], The compound $4SbBr_3 7py$, reported by Watari and Kinumaki[174] is probably an impure

sample of the bis adduct. Compounds $SbCl_3 2py$ and $BiCl_3 2py$ could not be obtained and it is probably significant that the reported analytical data for these complexes are not in close agreement with these formulations[174,178]. Instead antimony trichloride gave $SbCl_3 py$(mp185°), but if the product was not dried under vacuum the complex, $2SbCl_3 3py$(mp185°), with a distinctive X-ray powder pattern, was obtained. This latter complex contains only coordinated pyridine as shown by the absence of an infrared band at 601 cm^{-1}. Free pyridine can be detected if it is present[185]. On heating the complex loses pyridine to give the more stable mono-adduct. With bismuth trichloride, $2BiCl_3 3py$ was obtained, which unlike $2SbCl_3 3py$ showed no tendency to lose pyridine. Both these adducts behave as 1:1 electrolytes in nitrobenzene (Λ_m = 28.8 for $2SbCl_3 3py$)*. Neither $AsI_3 2py$[174] nor $AsI_3 3py$[175] were obtained under the experimental conditions used, but the possibility of their existence was not examined exhaustively. From this system, a mono-adduct $AsI_3 py$, was isolated.

* (Λ_m = 28.3 $ohm^{-1} mole^{-1} cm^2$ for $2BiCl_3 3py$)

2,2',2"-Terpyridyl Complexes

As found in other groups[186], the tridentate terpyridyl ligand, emphasises differences in the coordination

behaviour of the acceptor molecules. In all cases, the ligand was reacted in equimolar ratios with the trihalide, but the combining ratios varied (Table 2). Although $2AsCl_3$.terpy was produced from such a reaction, an analytically pure sample was only obtained using excess trichloride. The arsenic compounds are 1:1 electrolytes and the antimony compounds 2:1 electrolytes in nitrobenzene. Solutions of $BiCl_3$terpy are essentially nonconducting.

TABLE 2

Group VB Trihalide Terpyridyl Complexes

Complex	Λ_m in $PhNO_2$[a] (ohm^{-1} $mole^{-1}$ cm^2)	Formulation
$2AsCl_3$.terpy	28.6	$[AsCl_2terpy^+]AsCl_4^-$
$AsBr_3$.terpy	24.3	$[AsBr_2terpy^+]Br^-$
$3SbCl_3$.2terpy	41.1	$2[SbCl_2terpy^+]SbCl_5^-$
$3SbBr_3$.2terpy	35.8	$2[SbBr_2terpy^+]SbBr_5^-$
$3SbI_3$.2terpy	36.3	$2[SbI_2terpy^+]SbI_5^-$
$BiCl_3$.terpy	b	$[BiCl_3terpy]$

[a] At 10^{-3}M for arsenic complexes; at 0.3×10^{-3}M for antimony complexes;

[b] Insoluble in $PhNO_2$, Λ_m = 5.7 in dimethylformamide.

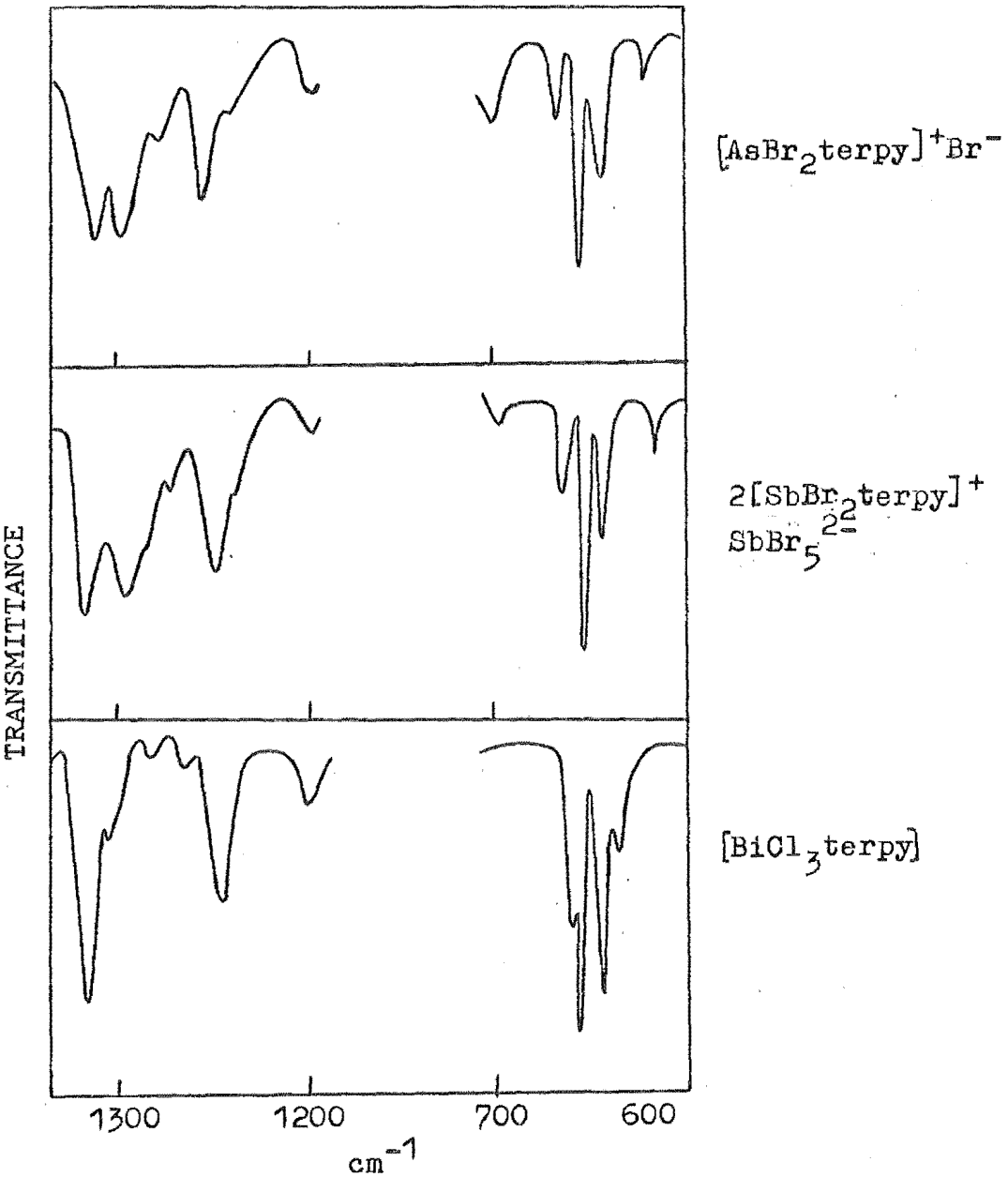


FIGURE 2. Infrared spectra of terpyridyl complexes.

The formulations indicated by these conductivities require the arsenic and antimony complexes to contain five-coordinate cations, $[MX_2terpy^+]$, associated with varying anions. The infrared spectra (above 600 cm^{-1}) of the arsenic and antimony compounds, for which this cation is postulated, all show identical ligand bands, while that from the bismuth complex shows distinct differences. This is especially apparent in the regions which show the greatest changes on coordination (Figure 2). As expected from these formulations, a wide variety of metal-halogen stretching modes is observed (Table 6). When compared with the bands from the $MX_3 2L'$ and $MX_3 L''$ complexes, the M-X bands for the terpyridyl complexes are unusually broad and complex with poorly defined shoulders superimposed upon the resolved components. Confirmation of the presence of the $SbCl_5^{2-}$ anion in the crystalline complex, $3SbCl_3 2terpy$, is obtained from ultraviolet reflectance spectra (Table 3). Both the terpyridyl complex and $(NH_4)_2SbCl_5$ show a characteristic shoulder at 360 mμ. The reaction of terpyridyl with these trihalides clearly indicates the strong preference of arsenic and antimony for five-fold coordination. That arsenic adopts five-fold coordination less readily is indicated

TABLE 3

Diffuse Reflectance Spectra ($\lambda > 300m\mu$) for $SbCl_3$ complexes

Complex	Band maxima ($m\mu$)
$(NH_4)_2SbCl_5$	325, 360(sh)
$3SbCl_3.2terpy$	335, 360(sh)
$SbCl_3.dipy$	310
$SbCl_3 2Ph_3AsO$	315
$SbCl_3 2pyO$	315

by the non-formation of an AsX_5^{2-} anion from equimolar reactions of the halide and ligand. The reluctance of $BiCl_3.terpy$ to ionize off a chloride ion can be correlated with the increasing tolerance of the heavier elements for high coordination numbers.

The reaction of terpyridyl with the Group VB halides may be compared with the analogous reactions with the Group IVB elements[186], where again differences in acceptor properties can be related to the preference for higher coordination numbers at the bottom of the group. The complexes formed with the tetrahalides involve six-coordinate cations (Table 4). In contrast to $AsCl_3$, $GeCl_4$ fails to react with terpyridyl. This can be attributed to greater difficulty in ionizing the halogen rather than to lower acceptor properties.

TABLE 4

Group IVB Tetrahalide Terpyridyl Complexes[a]

Complex	Λ_m in $PhNO_2$ ($ohm^{-1}mole^{-1}cm^2$)	Formulation
GeI_4.terpy	24.2	$[GeI_3terpy^+]I^-$
$3SnCl_4$.2terpy	37.3	$2[SnCl_3terpy^+]SnCl_6^{2-}$
$3SnBr_4$.2terpy	b	$2[SnBr_3terpy^+]SnBr_6^{2-}$
SnI_4.terpy	23.2	$[SnI_3terpy^+]I^-$

[a] From ref. 186

[b] Insoluble in $PhNO_2$

For example germanium readily gives $GeCl_4$dipy a six-coordinate complex[186]. However the ionization of this complex in nitrobenzene is considerably lower than that of its arsenic analogue (Λ_m = 0.7 for $GeCl_4$dipy [186] and 19.0 ohm^{-1} $mole^{-1}$ cm^2 for $AsCl_3$dipy [170]).

Pyridine N-Oxide and Triphenylarsine Oxide Complexes

Although a number of oxo-ligand complexes of the Group VB trihalides are known[159], no pyridine N-oxide complexes have been reported, and only one arsine oxide complex. In the present work it was found that these ligands differ from pyridine and the tertiary amines

in yielding a more extensive range of 1:2 adducts. Since the iodides are unstable through oxidation by the ligands, complexes could not be prepared from arsenic triiodide and pyridine N-oxide, or from antimony triiodide and triphenylarsine oxide. Although $SbI_3 2pyO$ is unstable, it was isolated. Bis complexes were also obtained from reactions of the amine oxide with arsenic and antimony trichlorides and tribromides, and from the arsine oxide with antimony and bismuth trichlorides and tribromides. X-ray powder photographs show $AsCl_3 2pyO$ and $SbCl_3 2pyO$ to be isomorphous. The reaction of bismuth trichloride and pyridine N-oxide always gave $2BiCl_3 5pyO$, even when excess halide was used. This complex is a nonelectrolyte (Λ_m = 3.5 ohm^{-1} $mole^{-1}$ cm^2 in dimethylformamide) but is of unknown constitution.

Both the pyridine N-oxide and triphenylarsine oxide complexes are partially ionized in nitrobenzene (Table 5). The molar conductivities, which become significant, show the same trends as reported by Roper and Wilkins[170] for the MX_3dipy complexes; that is dissociation increasing from chlorides to iodides but decreasing from arsenic to bismuth. For the dipyridyl complexes there is evidence in specific cases for partial ionization of the type

TABLE 5

Λ_m for Group VB Trihalide Oxo-Complexes[a]

(a) Pyridine N-Oxide Complexes			
$AsCl_3 2pyO$	5.0	$AsBr_3 2pyO$	11.0
$SbCl_3 2pyO$	5.9	$SbBr_3 2pyO$	b
(b) Triphenylarsine Oxide Complexes			
$SbCl_3 2Ph_3AsO$	10.8[c]	$SbBr_3 2Ph_3AsO$	13.5
$BiCl_3 2Ph_3AsO$	6.5	$BiBr_3 2Ph_3AsO$	6.9

[a] At 10^{-3}M

[b] Decomposed in $PhNO_2$ as did $SbI_3 2pyO$

[c] Ref. 32 gives Λ_m = 10.4 $ohm^{-1}mole^{-1}cm^2$

$$MX_3dipy \rightleftharpoons [MX_2dipy^+] + X^-$$

Similarly Phillips and Tyree[32] have suggested the ionization

$$SbCl_3 2Ph_3AsO \rightleftharpoons [SbCl_2 2Ph_3AsO]^+ + Cl^-$$

to explain the conductivity of $SbCl_3 2Ph_3AsO$. This complex has a square pyramidal structure with the ligands in cis basal positions[159] and yet in nitrobenzene Λ_m is 10.8 ohm^{-1} $mole^{-1}$ cm^2. The bis-pyridine complexes also show significant Λ_m values ($AsBr_3 2py$, 11.5; $SbBr_3 2py$, 15.7 $ohm^{-1} mole^{-1} cm^2$; $BiBr_3 2py$, insoluble). It is therefore considered that although the $MX_3 2L'$ and $MX_3 L''$ complexes are partially ionized in solution, they are covalent in the crystalline state.

INFRARED STUDIES

Group VB Trihalide Complexes

Although recent far infrared studies have led to the assignment of metal-ligand vibrations for a variety of complexes, no assignments appear to have been made for the complexes of the Group VB trihalides. Previous infrared studies on these complexes have generally been confined to the region above 600 cm^{-1}. Various pyridine complexes have been studied by Watari and Kinumaki[174].

Assignment of the P-O stretching frequency for $MX_3 2Ph_3PO$ complexes has been made by Frazer et al[179], and for other trihalide phosphine oxide complexes by Zackrisson and Alden[182]. Phillips and Tyree[32] have assigned ν(As-O) for $SbCl_3 2Ph_3AsO$. An infrared and Raman study has been carried out on $(NH_4)_2SbCl_5$[187].

In the present work, the assignment of metal-ligand frequencies has been approached using the MX_3dipy series. Confirmation of assignments has been obtained by comparing the results with those from the bis pyridine N-oxide and triphenylarsine oxide complexes. For a more general comparison with the dipyridyl adducts, the spectra of the pyridine and terpyridyl compounds have been investigated.

The infrared spectra of the complexes above 500cm^{-1} are typical of the coordinated ligands and the ν(N-O) and ν(As-O) modes show the usual displacements[32,188]. In the region below 500 cm^{-1} bands assignable to metal-ligand and metal-halogen stretching vibrations are found. Bands below 180 cm^{-1} are sometimes more difficult to interpret since lattice modes and bending vibrations are also expected to occur. Metal-halogen stretching vibrations can be identified as strong bands which shift to lower frequencies as the mass of the halogen

increases. The assignment of metal-ligand stretching modes is discussed in the following sections.

Metal-Ligand Stretching Frequencies

1. Dipyridyl Complexes Free dipyridyl has bands at 427 and 401 cm^{-1} (out of plane ring deformation[189]). On coordination these bands generally split and move to higher frequencies and a new weak band, believed to be a ligand mode, appears at about 350 cm^{-1}. In the 285 - 185 cm^{-1} region two medium bands are observed which are additional to the ligand bands and distinct from the metal-halogen frequencies (Table 6). These bands move systematically to lower frequencies as the atomic number of the acceptor atom or the halogen is increased, and are therefore assigned as metal-dipyridyl stretching modes, ν(M-N). The displacement of the band to lower frequencies with decreasing electronegativity. of the halogen indicates a progressive decrease in the metal-nitrogen bond strength. There is no evidence that the ν(M-N) bands occur below 180 cm^{-1}. The band which occurs at 166 cm^{-1} in the free ligand is replaced by others at lower frequencies. A very weak band (104 - 113 cm^{-1}) occurring in most of the complexes is probably an activated ligand vibration or a lattice mode.

For the dipyridyl complexes of arsenic and antimony trichloride, ν(M-N) and ν(M-X) occur at similar frequencies. Therefore the only meaningful assignment of the bands in the 340 - 270 cm^{-1} region for $AsCl_3$dipy is ν(As-Cl) + ν(As-N). However comparison of the ν(Sb-Cl) frequencies for the dipyridyl and oxo-ligand complexes suggests the bands at 282, 266 cm^{-1} in the $SbCl_3$dipy spectrum can be assigned as ν(Sb-N).

2. Pyridine N-Oxide and Triphenylarsine Oxide Complexes

For the oxo-ligand complexes medium strength bands in the 390 - 310 cm^{-1} region (Table 7) can be identified as metal-ligand stretching modes, ν(M-O). These bands show progressive shifts to lower frequencies as the electronegativity of the halogen decreases. The observation of only one ν(M-O) band for the pyridine N-oxide complexes cannot be considered adequate evidence for a trans configuration, especially since ν(N-O) generally shows two components. The ν(M-O) band for $SbCl_3 2Ph_3AsO$, which is known to have the ligands in cis basal positions, does show two components. However for the other arsine oxide complexes ν(M-O) is partially obscured by the strong arsenic-phenyl band of the ligand[190], at 360 - 350 cm^{-1}. The remaining ligand bands (Table 7) do not interfere with the assignments

of metal-halogen or metal-ligand stretching vibrations.

3. Pyridine Complexes Uncoordinated pyridine has one band at 403 cm^{-1} (out of plane ring deformation[90]) which moves to higher frequencies on coordination. For the bis-complexes assignment of metal-pyridine stretching vibrations, ν(M-N), is possible only for $SbBr_3$2py. For $AsBr_3$2py, ν(As-N) and ν(As-Br) occur at similar frequencies and the poor resolution of the $BiBr_3$2py spectrum prevents assignment of its bands. The metal-ligand vibrations for $SbBr_3$2py (Table 6) occur at 250, 230 cm^{-1}, slightly lower than for the corresponding dipyridyl complex.

4. Terpyridyl Complexes Free terpyridyl has bands at 417 and 401 cm^{-1} which can be attributed to ring type vibrations. On coordination these bands split and move to higher frequencies. The spectrum of the uncoordinated ligand also shows extremely weak bands in the 280 - 220 cm^{-1} region, a strong band at 185 cm^{-1} and a medium band at 120 cm^{-1}. The assignment of metal-ligand vibrations for terpyridyl complexes must be regarded as tentative since the free ligand has weak bands in the region where these modes may be expected to occur. These ligand bands may become more intense

on coordination and coupling of metal-ligand modes with other vibrations is most probable. It is suggested that medium strength bands in the 280 - 240 cm^{-1} region are essentially ν(M-N) absorptions (Table 6). Weak bands which occur above 300 cm^{-1} on coordination, have also been observed in zinc-terpyridyl complexes[191], and are probably activated ligand absorptions.

Metal-Halogen Stretching Frequencies

The ν(M-X) absorptions are broad, poorly resolved bands which move systematically to lower frequencies with increasing atomic number of M or X. As for transition metal[2,62] and tin[192] complexes, the metal-bromine stretching frequencies, ν(M-Br), occur at 0.65 - 0.80 of the frequency of a directly analogous ν(M-Cl) vibration. The ν(M-I): ν(M-Cl) ratio is 0.55 - 0.65. The metal-halogen stretching frequencies of the free trihalides[193] are lowered considerably on coordination. For example, a decrease of over 100 cm^{-1} is observed for the antimony trichloride complexes. This can be correlated with increased Sb-Cl distances. The average Sb-Cl distance in antimony trichloride is 2.36 Å [194], while for $SbCl_3 2Ph_3AsO$ it is 2.46 Å [159]. Increased electron density about the acceptor atom and a change in hybridisation on adduct formation would cause a weakening

TABLE 6a

Infrared Spectra (500 - 100 cm^{-1}) of Nitrogen Ligand Complexes of the Group VB Trihalides[a]

Compound	ν(M-N)	ν(M-X)	Other Bands
Pyridine	-	-	403m[b]
$AsBr_3$2py	c	254sh, ~ 200sbr	420w, 400w[b]
$SbBr_3$2py	250sh, 230m	189sh, 162s	416m, 144s, 119w, 107w
Dipyridyl (2,2')	-	-	427w, 404m, 166m, 140sh
$AsCl_3$dipy	c	340sh, 317s, 304sh, 273s	466vw, 444w, 422w, 411m, 235m[b]
$AsBr_3$dipy	285s, 254s	218sh, 203s, 170s	469vw, 441vw, 402vw, 347w, 143s, 136m, 107w
AsI_3dipy	255m, 252m	196s, 182s, 160s	479w, 449w, 400w, 346m, 135m
$SbCl_3$dipy	282m, 266m	241s, 220s, 200sh	462vw, 442vw, 421w, 406m, 359vw, 338vw, 147m, 104vw
$SbBr_3$dipy	251m, 242m	189s, 167s	465vw, 434vw, 418vw, 407w, 357w, 133m, 127m
SbI_3dipy	224m, 212w	164sh, 145s	457vw, 438vw, 427vw, 405m, 350w, 334w, 134sh, 109w
$BiCl_3$dipy	259m, 232m	173sbr	457w, 440vw, 414m, 403w, 348w, 159s, 128m, 113w
$BiBr_3$dipy	214m, 190s	124sbr	461w, 425w, 404m, 346m, 158m, 146sh, 102m
BiI_3dipy	214m, 185m	-	452w, 424w, 418w, 404m, 344m, 145s, 122m, 104w

[a] As Nujol mulls

[b] Not recorded below 200 cm^{-1}

[c] ν(M-N) obscured by ν(M-X).

TABLE 6b

Infrared Spectra (500 - 100 cm^{-1}) of Group VB Trihalide Terpyridyl Complexes[a]

Compound	ν(M-N)	ν(M-X)[d]	Other Bands
Terpyridyl	-	-	417vw, 401m, 185m, 120m
$2AsCl_3$terpy	c	364s, 334s, 283s	444w, 416vw, 407m, 240m[b]
$AsBr_3$terpy	272sh, 260m(?)	215 sbr	467w, 436vw, 411m[b]
$3SbCl_3$terpy[e]	c	284sh, 260s, 220s	466vw, 440w, 407m, 324w, 172m, 149m, 118sh.
$3SbBr_3$terpy	260m, 255sh	189s, 170s	466vw, 435w, 407m, 317w, 141m, 129sh
$BiCl_3$terpy	250sh, 238sh(?)	189sbr, 179sh	414vw, 403m, 302w, 135m, 124m
$3SbI_3$terpy	258m, 253sh	147s, 134s	466vw, 424w, 404m, 312w, 179m

[a] As Nujol mulls

[b] Not recorded below 200 cm^{-1}

[c] ν(M-N) obscured by ν(M-Cl).

[d] ν(M-X) broad complex bands

[e] $(NH_4)_2SbCl_5$ has ν(M-Cl) at 290,260,230.

Parallel figures on pure compounds (1969)

TABLE 7

Infrared Spectra (500 - 100 cm^{-1}) of Oxygen Ligand Complexes of the Group VB Trihalides [a]

Compound	ν(M-O)	ν(M-X)	Other Bands
Ph_3AsO	382sh, 372m	225s, 207m, 186s	476s, 469s, 452m, 403vw, 352s[b], 322vw, 282vw, 265vw, 242w, 152m, 121w
$SbCl_3 2Ph_3AsO$	387sh, 375s	220s, 190s	478s, 468s, 461sh, 400vw, 355s, 336sh, 290w, 261w, 248w, 135m, 121w
$SbBr_3 2Ph_3AsO$	364s[c]	155s	476m, 465m, 453sh, 400vw, 359s, 349sh, 288w, 254vw, 244vw, 145sbr, 111w
$BiCl_3 2Ph_3AsO$	369m[c]	185sbr	480s, 473s, 460m, 407w, 352m, 325sh, 250wbr, 142m, 121sh
$BiBr_3 2Ph_3AsO$	362m[c]	-	480s, 472s, 460m, 405vw, 352m, 325sh, 255wbr[d]
pyO	-	-	469s, 454sh, 235m
$AsCl_3 2pyO$	375m	327s, 307s, 287s	482m, 449m, 230m[d]
$AsBr_3 2pyO$	359m	251sh, < 200sbr	482m, 448m, 305m[d]
$SbCl_3 2pyO$	391m	259s, 237s, 200s	466m, 445w, 305w, 137m, 112sh
$SbBr_3 2pyO$	353m	185s, 172sh	488m, 442m, 301vw, 274w, 133m, 120sh
$SbI_3 2pyO$	308mbr	-	485m, 460w, 439w[d]
$2BiCl_3 5pyO$	331sh, 300m	-	464m, 455m, 225mbr[d]

[a] As Nujol mulls

[b] Arsenic-phenyl stretching vibration

[c] Shoulder on ν(arsenic-phenyl)

[d] Not recorded below 200 cm^{-1}

of the metal-halogen bond. The lowering of ν(M-X) frequencies with increased coordination is a general trend, and has been observed previously in a variety of cases[189].

Group IVB Tetrahalide Complexes

The identification of metal-ligand stretching frequencies for pyridine and dipyridyl complexes of Group VB trihalides, prompted an examination of the spectra of some germanium and tin tetrahalide adducts. Metal-halogen stretching vibrations have previously been assigned for the complexes $GeCl_4$dipy, $SnCl_4$dipy and $SnCl_4$2py by Beattie et al.,[195] however since measurements were only made to 250 cm^{-1} metal-ligand modes were not identified. In the present work metal-halogen and metal-ligand vibrations have been assigned (Table 8). After this work was completed an independent examination of the spectra of the SnX_4dipy complexes was published by Farona and Grasselli[196]. Their spectral frequencies and assignments essentially agree with the present work.

1. Dipyridyl Complexes The metal-dipyridyl stretching vibrations are assigned to the medium strength bands occurring in the 250 - 240 cm^{-1} range. For

TABLE 8

Infrared Spectra (350 - 200 cm^{-1}) of Tin Complexes

Compound	ν(M-N)	ν(M-X)
$GeCl_4$dipy	241m	330sbr, 297m
$SnCl_4$dipy	250m	325sbr, 303sh, 280m
$SnBr_4$dipy	a	258s[b], 239s, 218m
SnI_4dipy	248m	-
$SnCl_4$2py	229sh, 223m	323sbr, 303sh, 282m
$SnBr_4$2py	a	244s, 228s, 215m

[a] ν(M-N) obscured by ν(M-X)

$SnBr_4$dipy, ν(Sn-N) and ν(Sn-Br) occur at similar frequencies and therefore separate assignment of ν(Sn-N) is not possible, although Farona and Grasselli have assigned the highest energy component of the three bands to this mode[196].

2. Pyridine Complexes For the $SnCl_4$2py complex the bands at 229, 223 cm^{-1} are assigned to the metal-ligand stretching vibrations. The analogous mode for $SnCl_4$dipy lies at slightly higher frequencies. For these two compounds the ν(Sn-Cl) bands are clearly multiple, and closely similar in profile and position, thus indicating the $SnCl_4$2py complex has a cis configuration. For a trans complex only one ν(Sn-Cl) band is allowed in the infrared, whereas for a cis complex four ν(Sn-Cl) bands are allowed[197]. Beattie et al[195] apparently observed only one ν(Sn-Cl) component and therefore assigned a trans configuration to the pyridine complex. As for the corresponding dipyridyl complex separate assignment of the ν(Sn-N) and ν(Sn-Br) modes for $SnBr_4$2py is not possible.

Comparison of Metal-Halogen Frequencies for Complexes of the Group IVB and VB Halides

In the present work metal-ligand and metal-halogen

stretching vibrations have been assigned for a range of Group IVB and VB halide complexes. The average values of these vibrations are listed in Table 9, along with values for Group IVB oxo-adducts, whose infrared spectra have been assigned previously[190,198,201]. The complexes are all of the type MX_n2L' or MX_nL'' (n = 3 or 4; L' = mono-, L'' = bidentate ligand). The Group IVB complexes are presumably octahedral and the VB complexes pseudo-octahedral, the lone pair of electrons occupying the sixth position. For the arsenic and antimony adducts the ν(M-L) frequencies fall in the same range as for the corresponding germanium and tin compounds. However the values for ν(Sb-X) are considerably lower than those for ν(Sn-X). The lower ν(Sb-X) frequencies can be correlated with greater average Sb-X bond lengths. For example the average M-Cl distances in $(NH_4)_2SnCl_6$ and $(NH_4)_2SbCl_5$ are 2.41 Å [205] and 2.57 Å [158] respectively.

For arsenic and germanium halide complexes, infrared data is limited. Although As-Cl and Ge-Cl stretching frequencies appear to occur in the same region, As-Br frequencies are lower than the only reported Ge-Br frequency (Table 9).

TABLE 9

Comparison of ν(M-X)[a] and ν(M-L)[a] for Group IVB and VB Halide Complexes

Compound	ν(M-X)	ν(M-L)	Compound	ν(M-X)	ν(M-L)
$GeCl_4$2pyO	320	402	$AsCl_3$2pyO	307	375
$GeCl_4$dipy	319	241	$AsCl_3$dipy	308	-
Cs_2GeCl_6	310	-			
$(NEt_4)_2GeCl_6$	293	-			
$GeCl_2$acac	322	-			
$GeBr_2$acac	270	-	$AsBr_3$dipy	197	270
$SnCl_4$2pyO	313	382	$SbCl_3$2pyO	232	391
$SnCl_4$2Ph_3AsO	307	392	$SbCl_3$2Ph_3AsO	200	379
$SnCl_4$dipy	308	250	$SbCl_3$dipy	225	274
Cs_2SnCl_6	310	-	$(NH_4)_2SbCl_5$	260	-
$(NEt_4)_2SnCl_6$		-			
$SnBr_4$2pyO	221	372	$SbBr_3$2pyO	180	353
$SnBr_4$2Ph_3AsO	217	393	$SbBr_3$2Ph_3AsO	155	364
$SnBr_4$dipy	238	-	$SbBr_3$dipy	178	247
$SnBr_4$2py	229	-	$SbBr_3$2py	171	237
SnI_4dipy	181	248	SbI_3dipy	149	220

[a] Average values; from this work and refs. 190,195,196,198-204.

Review of Metal-Ligand Frequencies for Related Complexes

Metal-ligand stretching vibrations have been assigned previously for transition metal and tin complexes of triphenylarsine oxide and pyridine N-oxide. For triphenylarsine oxide complexes ν(M-L) frequencies lie in the 440 - 370 cm^{-1} range[9,190] and for pyridine N-oxide complexes, between 450 and 300 cm^{-1} [20,201,202]. The metal-ligand bands for the bidentate analogue of pyridine N-oxide (2,2'-dipyridine N,N'-dioxide) occur at similar frequencies[206]. Metal-pyridine vibrations for transition metal complexes have been identified below 290 cm^{-1} [90,191,207,208,209], but no assignments had been made for p-block complexes. Several metal-terpyridyl stretching vibrations would be expected, although no evidence was found for such modes for rare earth complexes[210]. Bands at 243 - 245 cm^{-1} in the spectra of Zn(terpy)X_2 (X = Cl, Br, I) complexes have been attributed to ν(M-N) vibrations[191]. Such assignments must be regarded as tentative since the use of a chelate ligand introduces complications associated with ring vibrations.

There has been some uncertainty over the assignment of metal-dipyridyl stretching vibrations. Absorptions attributable to this mode have been found in the 300 -

200 cm^{-1} region for transition metal and rare earth complexes. Bands between 300 and 250 cm^{-1} have been assigned to ν(M-N) modes for the tris dipyridyl complexes of Cu(II), Ni(II) and Zn[211]. Similar assignments have been made for other Cu(II) dipyridyl compounds[212,213] and for M(dipy)X_2 (M = Pd, Zn; X = Cl, Br, I) complexes[191,209]. For a series of rare earth complexes of dipyridyl the ν(M-N) frequencies (290 - 210 cm^{-1}) were related to the polarizing power of the cation[214]. However, Clark and Williams[215] consider that for the cations of the type $M(dipy)_3^{2+}$ (M = Mn, Fe, Co, Ni) and $M(dipy)_3^{3+}$ (M = Fe, Co) bands between 282 and 228 cm^{-1} are ligand modes activated by the crystal field on coordination. No bands were observed in this region for the low spin complexes $[Fe(dipy)_3]Cl_2.6H_2O$, $[Fe(dipy)_3](ClO_4)_3.3H_2O$ and $[Co(dipy)_3](ClO_4)_3.3H_2O$. Both spin-pairing and an increase in oxidation state, increases metal-ligand modes[2,62] so that for these complexes they would be expected to occur above 300 cm^{-1}. It may be that for the three low-spin complexes studied the ν(M-L) band is very weak and has not been observed[216]. A comparison may be made with the octahedral hexamine complexes where ν(M-N) is strong (at 334 - 298 cm^{-1}) for the

divalent complexes but very weak (at 499 - 449 cm^{-1}) for the trivalent complexes[217]. For the high-spin series $[M(dipy)_3]Br_2$, the bands follow the expected trend for a ν(M-L) mode; that is an increase in frequency on going from Mn (228 cm^{-1}) to Co (261cm^{-1}) to Ni (282cm^{-1}). This order has been found for a number of oxygen[20,206] and nitrogen donor[90,217] complexes. It is therefore considered that these bands are essentially metal-dipyridyl stretching modes. For alkyl tin halide complexes of dipyridyl ν(M-N) modes have not been observed[189], however they would be expected to occur below 200 cm^{-1}.

Further support for the assignment of metal-dipyridyl stretching vibration to the absorptions between 300 and 200 cm^{-1} is obtained from the Group VB trihalide complexes. Metal-ligand modes fall in the same general region for transition metal and Group VB trihalide complexes. However, unlike transition metal halide complexes[9,19,90,191] the ν(M-L) bands for the VB halide adducts show a systematic decrease in frequency as the electronegativity of the halogen is decreased, indicating the importance of the inductive effect in such complexes (Table 10).

TABLE 10

Comparison of ν(M-L)[a] for Group VB and Transition Metal Halide Complexes

Compound	ν(M-L)	Compound	ν(M-L)
$SbCl_3$dipy	274	$ZnCl_2$dipy	241
$SbBr_3$dipy	247	$ZnBr_2$dipy	250
SbI_3dipy	220	ZnI_2dipy	250
$SbCl_3$2pyO	391	$CoCl_2$2Me_3NO	568
$SbBr_3$2pyO	353	$CoBr_2$2Me_3NO	564
$SbI_3$2pyO	308		
$SbCl_3$2Ph_3AsO	379	$FeCl_2$2Ph_3AsO	384
$SbBr_3$2Ph_3AsO	364	$FeBr_2$2Ph_3AsO	399

[a] Average values; from this work and refs. 9,19,191.

EXPERIMENTAL

PREPARATION OF COMPLEXES

The preparation and all handling of the complexes was carried out in a dry box. Volatile reaction components were manipulated using a vacuum line. Generally complexes were prepared by the direct combination of stoichiometric ratios of the ligand and trihalide in anhydrous solvents. Procedures used for drying the solvents are described in Chapter 4. After collection on a sintered-glass crucible, the adducts were washed with pure solvent, followed by petroleum ether (50 - 70°), and pumped dry under high vacuum. Since the arsenic complexes usually suffer immediate hydrolysis on exposure to air, they were handled only in rigorously anhydrous conditions. Antimony and bismuth complexes were found to be more stable.

Arsenic trichloride, arsenic tribromide, antimony trichloride and antimony tribromide were distilled immediately before use. Bismuth trichloride was sublimed in vacuo and freshly opened reagent grade samples of the remaining trihalides were used as received.

1. Pyridine Complexes

'Analar' grade pyridine was dried over potassium hydroxide and fractionally distilled. The fraction

boiling at 114.7 - 115° was collected and stored over barium oxide. Generally the pyridine complexes were prepared by distilling toluene and excess pyridine from a vacuum line onto the metal salt. The reaction tube was sealed under vacuum and shaken for two days, whereupon it was transferred to a dry box. The product was washed by decantation with toluene and petroleum ether (50 - 70°). Excess solvents were removed by reattaching the tube to the vacuum line and pumping off for a short period (< five minutes).

Tribromobis(pyridine)arsenic(III)

A yellow powder was formed from arsenic tribromide (0.93g.) and pyridine (5 ml). The complex is rapidly hydrolysed in air. X-ray powder photographs show arsenic(III) oxide to be a decomposition product. Melting point: 195°. Found: C, 25.9; H, 2.8; Br, 50.6. $C_{10}H_{10}AsBr_3N_2$ requires C, 25.4; H, 2.1; Br, 50.7%.

Triiodo(pyridine)arsenic(III)

Arsenic triiodide (1.01g.) and pyridine (5 ml) reacted to give an orange powder which decomposed on grinding. Found: C, 10.7; H, 0.97, I, 70.7. $C_5H_5AsI_3N$ requires C, 11.2; H, 0.94; I, 71.4%.

Trichloro(pyridine)antimony(III)

This was prepared as a white precipitate from antimony trichloride (0.60g.) and pyridine (1ml). Melting point: 185°. Found: C, 19.5; H, 2.0; Cl, 34.0. $C_5H_5Cl_3NSb$ requires C, 19.5; H, 1.6; Cl, 34.6%.

Hexachlorotris(pyridine)diantimony(III)

When pyridine (7 ml) was distilled directly onto antimony trichloride (1.08g.) without additional solvent the trihalide dissolved to give a colourless solution. As pyridine was pumped off a viscous product formed which solidified on the addition of petroleum ether (50 - 70°). The white complex was not pumped off. Melting point: 185°. Because the complex rapidly loses pyridine carbon analyses were always low. Chloride however was determined immediately after preparation. Found: C, 24.1 (24 hours later: 22.9); H, 2.2; Cl, 30.7; $C_{15}H_{15}Cl_6N_3Sb_2$ requires C, 25.9; H, 2.2; Cl, 30.7%.

Tribromobis(pyridine)antimony(III)

Reaction of antimony tribromide (1.15g.) and pyridine (5 ml) gave a yellow complex. Found: C, 24.5; H, 2.6; Br, 46.2. $C_{10}H_{10}Br_3N_2Sb$ requires C, 23.1, H, 1.9; Br, 46.1%.

Hexachlorotris(pyridine)dibismuth(III)

A white powder formed from bismuth trichloride (1.42g.) and pyridine (6 ml). Loss of weight on pumping for 5 hours: 0.8%. Found: C, 20.6; H, 1.9; Cl, 24.1. $C_{15}H_{15}Bi_2Cl_6N_3$ requires C, 20.7; H, 1.7; Cl, 24.5%.

Tribromobis(pyridine)bismuth(III)

Pyridine (5 ml) was distilled directly onto bismuth tribromide (0.52g.). Addition of petroleum ether (50 - 70°) gave a yellow complex. Found: C, 20.8; H, 2.1; Br, 39.7. $C_{10}H_{10}Br_3BiN_2$ requires C, 19.8; H, 1.7; Br, 39.5%.

2. 2,2'-Dipyridyl Complexes

Samples of the dipyridyl adducts of arsenic tribromide and the bismuth trihalides prepared by Roper[218] were used. The remaining dipyridyl complexes were prepared according to Roper and Wilkins[170]. The dipyridyl was dried over phosphorus pentoxide.

Trichloro(2,2'-dipyridyl)arsenic(III)

Arsenic trichloride (1.5g.) was distilled from a vacuum line onto a frozen solution of dipyridyl (1.21g.)

in benzene. Reaction occurred on warming. The yellow complex was transferred to a dry box for collection and washing. Found: Cl, 31.9. $C_{10}H_8AsCl_3N_2$ requires Cl, 31.6%.

Triiodo(2,2'-dipyridyl)arsenic(III)

A brown precipitate formed on mixing toluene solutions of arsenic triiodide (0.82g.) and dipyridyl (0.28g.). Found: I, 62.4. $C_{18}H_8AsI_3N_2$ requires I, 62.2%.

Trichloro(2,2'-dipyridyl)antimony(III)

This was prepared as a cream precipitate from benzene solutions of antimony trichloride (1.03g.) and dipyridyl (0.70g.). Found: Cl, 27.2. $C_{10}H_8Cl_3N_2Sb$ requires Cl, 27.7%.

Tribromo(2,2'-dipyridyl)antimony(III)

Antimony tribromide (0.54g.) and dipyridyl (0.24g.) dissolved in toluene gave a bright yellow complex. Found: Br, 46.5. $C_{10}H_8Br_3N_2Sb$ requires Br, 46.3%.

Triodo(2,2'-dipyridyl)antimony(III)

This complex formed as a dark red powder from toluene solutions of antimony triiodide (0.57g.) and

dipyridyl (0.15g.). Found: I, 58.2 : $C_{10}H_8I_3N_2Sb$ requires I, 57.8.

3. 2,2',2"-Terpyridyl Complexes

2,2',2"-Terpyridyl was recrystallised from petroleum ether (50 - 70°), M.Pt. 88°. Generally the complexes were prepared by reacting the ligand and the trihalide in equimolar ratios.

Dichloro(2,2',2"-terpyridyl)arsenic(III) Tetrachloro-arsenite(III)

Excess arsenic trichloride (1.61g.) was distilled from a vacuum line onto a benzene solution of terpyridyl (0.49g.). An analytically pure yellow complex was isolated only after the reaction mixture had been shaken for 2 days. Found: C, 30.8; H, 2.0; Cl, 35.6. $C_{15}H_{11}As_2Cl_6N_3$ requires C, 30.2; H, 1.8; Cl, 35.7%. This complex was not obtained analytically pure if the reaction was carried out using the components in equimolar ratios.

Dibromo(2,2',2"-terpyridyl)arsenic(III) Bromide

An orange precipitate was obtained from toluene solutions of arsenic tribromide (0.50g.) and terpyridyl

(0.37g.). Found: Br, 43.5; $C_{15}H_{11}AsBr_3N_3$ requires Br, 43.8%.

Dichloro(2,2',2"-terpyridyl)antimony(III) Pentachloroantimonate(III)

Antimony trichloride (0.23g.) and terpyridyl (0.23g.) dissolved in toluene gave a yellow powder. Found: C, 30.5; H, 2.5; Cl, 27.8. $C_{30}H_{22}Cl_6N_6Sb_3$ requires C, 31.3; H, 1.9; Cl, 27.7%.

Dibromo(2,2',2"-terpyridyl)antimony(III) Pentabromoantimonate(III)

From toluene solutions of antimony tribromide (0.68g.) and terpyridyl (0.34g.) an orange complex was precipitated. Found: C, 23.9; H, 1.6; Br, 46.1. $C_{30}H_{22}Br_6N_6Sb_3$ requires C, 23.2; H, 1.4; Br, 46.4%.

Diiodo(2,2',2"-terpyridyl)antimony(III) Pentaiodoantimonate(III)

A dark red powder formed when antimony triiodide (0.50g.) and the ligand (0.23g.) were mixed in toluene. Found: C, 18.9; H, 1.3; I, 57.0. $C_{30}H_{22}I_6N_6Sb_3$ requires C, 18.2; H, 1.1; I, 57.9%.

Trichloro(2,2',2"-terpyridyl)bismuth(III)

Bismuth trichloride (0.64g.) and terpyridyl (0.47g.)

dissolved in acetone reacted to give a cream precipitate. Found: C, 32.9; H, 2.6; Cl, 19.1. $C_{15}H_{11}BiCl_3N_3$ requires C, 32.8; H, 2.0; Cl, 19.4%.

4. Pyridine N-Oxide Complexes

Pyridine N-oxide was distilled under high vacuum before use.

Trichlorobis(pyridine N-oxide) arsenic(III)

Arsenic trichloride (0.57g.) was distilled from a vacuum line onto a frozen benzene solution of pyridine N-oxide (0.74g.). On warming an oil separated, which solidified when stirred with petroleum ether (BP 55 - 115°). Found: C, 32.5; H, 3.3; Cl, 28.0. $C_{10}H_{10}AsCl_3N_2O_2$ requires C, 32.3; H, 2.7; Cl, 28.6%.

Tribromobis(pyridine N-oxide)arsenic(III)

This was formed as a pale yellow powder from toluene solutions of arsenic tribromide (1.52g.) and pyridine N-oxide (1.3g.). Found: C, 23.8; H, 2.4; Br, 47.3. $C_{10}H_{10}Br_3AsN_2O_2$ requires C, 23.8; H, 2.0; Br, 47.5%.

Reaction of pyridine N-oxide with arsenic triiodide

A brick-red precipitate formed from toluene

solutions of arsenic triiodide (0.67g.) and pyridine N-oxide (0.28g.). When isolated the complex rapidly decomposed, liberating iodine.

Trichlorobis(pyridine N-oxide)antimony(III)

Reaction between antimony trichloride (0.66g.) and pyridine N-oxide (0.75g.) dissolved in toluene, gave a white powder. Found: C, 29.0; H, 2.5; Cl, 25.9. $C_{10}H_{10}Cl_3N_2O_2Sb$ requires C, 28.7; H, 2.4; Cl, 25.4%.

Tribromobis(pyridine N-oxide)antimony(III)

A yellow precipitate formed from toluene solutions of antimony tribromide (0.52g.) and the ligand (0.30g.) Found: C, 21.4; H, 2.0; Br, 43.7. $C_{10}H_{10}Br_3N_2O_2Sb$ requires C, 21.8; H, 1.8; Br, 43.5%.

Triiodidobis(pyridine N-oxide)antimony(III)

This complex was prepared as above using antimony triiodide (1.0g.) and pyridine N-oxide (0.26g.). Found: C, 18.1; H, 1.7; I, 55.2. $C_{10}H_{10}I_3N_2O_2Sb$ requires C, 17.3; H, 1.4; I, 55.0%. After a week the bright orange complex had decomposed, liberating iodine.

Hexachloropentakis(pyridine N-oxide)dibismuth(III)

Bismuth trichloride (0.41g.) and pyridine N-oxide (0.2g.) reacted in acetone or tetrahydrofuran to give a pale yellow complex. Found: C, 27.1; H, 2.4; Cl, 19.4. $C_{25}H_{25}Bi_2Cl_6N_5O_5$ requires C, 27.1; H, 2.3; Cl, 19.2%. The same product was obtained from reactions involving a greater metal halide:ligand ratio.

5. Triphenylarsine Oxide Complexes

Trichlorobis(triphenylarsine oxide)antimony(III)

This complex has been reported by Phillips and Tyree[32]. Benzene solutions of antimony trichloride (0.42g.) and triphenylarsine oxide (1.22g.) were mixed. On standing overnight, colourless crystals deposited. Found: Cl, 12.3. $C_{36}H_{30}As_2Cl_3O_2Sb$ requires Cl, 12.2%.

Tribromobis(triphenylarsine oxide)antimony(III)

Antimony tribromide (1.00g.) and triphenylarsine oxide (2.27g.) dissolved in benzene gave a yellow oil, which solidified on the addition of petroleum ether (50 - 70). Found: C, 44.1; H, 3.2; Br, 23.1. $C_{36}H_{30}As_2Br_3O_2Sb$ requires C, 43.0; H, 3.0; Br, 23.8%.

Reaction of triphenylarsine oxide with antimony triiodide

An inhomogeneous product separated when acetone solutions of antimony triiodide (0.50g.) and triphenylarsine oxide (0.63g.) were mixed. The absence of a band assignable to ν(As-O) in the infrared spectra of the product indicates that reduction of the ligand had occurred.

Trichlorobis(triphenylarsine oxide)bismuth(III)

Bismuth trichloride (0.12g.) and triphenylarsine oxide (0.25g.) gave a white precipitate from benzene. Found: C, 43.9; H, 3.1; Cl, 11.9. $C_{36}H_{30}As_2BiCl_3O_2$ requires C, 45.0; H, 3.1; Cl, 11.1%.

Tribromobis(triphenylarsine oxide)bismuth(III)

This was formed as a pale yellow powder from acetone solutions of bismuth tribromide (0.53g.) and the ligand (0.76g.). Found: C, 40.0; H, 3.0; Br, 21.6. $C_{36}H_{30}As_2Br_3BiO_2$ requires C, 39.5; H, 2.8; Br, 21.9%.

6. Ammonium Pentachloroantimonate(III)

This was prepared according to Edstrand et al[158]. Antimony trichloride (1.82g.) was mixed with ammonium

chloride (0.57g.) in 1M. HCl. The solution was evaporated until crystallisation began and then placed in a vacuum desiccator over concentrated sulphuric acid for 20 hours. Found: Cl, 52.2. $H_8Cl_5N_2Sb$ requires Cl, 52.9%.

7. Tin Complexes

Samples of tin complexes that had been previously prepared in this department were used for the infrared studies.

PHYSICAL METHODS, ANALYSES, AND REAGENTS

The physical measurements were made as described in Chapter 4, Section I. Methods not mentioned previously are described below.

Infrared Spectra below 200 cm^{-1} were recorded on an R.I.I.C. interferometer by Dr B.P. Straughan, Newcastle-upon-Tyne, and on a laboratory built[219] (Physics Department, University of Canterbury) spectrometer.

Molar Conductivities for the solvents used in this section are:

Ion-type	Nitrobenzene	Dimethylformamide
1:1	20 - 30	60 - 80
1:2	35 - 55	110 - 130
1:3	70 - 80	160 - 180

Analyses After hydrolysing samples with water or sodium hydroxide solution, halide was determined using the Volhard titration[149].

Drying and Purification of Solvents

Benzene (A.R. grade) was dried over sodium. Dimethylformamide[220] was mixed with 10% by volume of benzene and the benzene-water azeotrope was distilled

off at 80°. The dimethylformamide was dried over barium oxide for 5 days, fractionally distilled under reduced pressure, and stored over molecular sieves.

Petroleum Ether was dried over sodium.

Nitrobenzene[221] was dried over calcium chloride and distilled under reduced pressure (below 50°). The nitrobenzene was stored over molecular sieves.

Tetrahydrofuran was fractionally distilled from lithium aluminium hydride (B.Pt 64 - 65°) and stored over sodium.

Toluene (A.R. grade) was dried over sodium.

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Contribution from the Chemistry Department, University of Canterbury, Christchurch, New Zealand

High-Spin Five-Coordinate $[ML_5]^{2+}$ and $[ML_4(ClO_4)]^+$ Complexes with Trimethylphosphine Oxide and Trimethylarsine Oxide

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The preparation of high-spin five-coordinate complexes of composition, $[ML_5]^{2+}$ and $[ML_4(ClO_4)]^+$, L = Me_3PO and Me_3AsO, is reported for a number of first row divalent transition metal ions. The spectra of these compounds can best be correlated with a basically square pyramidal structure. Five-coordination is considered to be stabilised by the packing requirements of these ligands. The particular sensitivity to moisture of the Me_3PO complexes is related to the attainment of six-fold coordination with the formation of $[ML_5(H_2O)]^{2+}$ complexes. Low-frequency infrared data are presented and comparisons made with data for related $[ML_4]^{2+}$ tetrahedral complexes.

Introduction

Although examples of five-coordinate bivalent first row transition metal complexes with polydentate ligands are becoming increasingly common, examples of corresponding complexes with monodentate ligands are few and ML_5 complexes with identical ligands are limited to low-spin species such as $Fe(CO)_5$, $[Ni(CN)_5]^{3-}$ and $[Co(CNCH_3)_5]^+$.[1] We have now prepared a range of high-spin $[ML_5]^{2+}$ complexes with the oxo ligands Me_3PO and Me_3AsO (Table I) and a related series of $[ML_4(ClO_4)]^+$ complexes has also been isolated. All of these complexes are readily obtained under anhydrous conditions—$[ML_5]^{2+}$ using a slight excess of the ligand in acetone while $[ML_4(ClO_4)]^+$ are favoured using a deficiency of ligand and ethanol as solvent. The compounds are generally sensitive to atmospheric moisture though with the $[ML_5]^{2+}$ series the trimethylarsine oxide derivatives are less sensitive than their phosphine oxide analogues. The complexes are all decomposed in solution except for $[Ni(Me_3AsO)_5](ClO_4)_2$ which is relatively stable in acetone. The range of five-coordinate complexes of both types extends from manganese to nickel, with the exception that it has not been possible to obtain the $[FeL_5]^{2+}$ and $[CoL_4(ClO_4)]^+$ compounds (Table I). An X-ray structure analysis of $[Ni(Me_3AsO)_5](ClO_4)_2$ is now being attempted in these laboratories.

Results and Discussion

X-ray powder photographs show that all the $[ML_5](ClO_4)_2$ complexes have the same structure, and electronic reflectance spectra for the cobalt and nickel compounds (Table II) indicate a structure approximating that of a square pyramid. The spectra more closely resemble those obtained for other complexes known from X-ray analysis to have this configuration rather than those from complexes of the trigonal bipyramidal class.[2] Representative spectra from the present series are shown with those of $[Co(Me_5dien)Cl_2]$ and $[Ni(Me_5dien)Cl_2]$[3] in Figure 1. The same basic structure is also suggested for the $[ML_4(ClO_4)]^+$ complexes. The spectra of $[Ni(Me_3AsO)_4(ClO_4)]ClO_4$ and $[Ni(Me_3AsO)_4(ClO_4)]BPh_4$ are very similar to that of $[Ni(Me_3AsO)_5](ClO_4)_2$ (Figure I) and the iron(II) and manganese(II) $ML_4(ClO_4)_2$ compounds (L = Me_3PO and Me_3AsO) can reliably be formulated in the same manner in view of the close similarity of their X-ray powder photographs to that of $[Ni(Me_3AsO)_4(ClO_4)]ClO_4$. The isolation of the tetraphenylboron complexes, for Fe^{II} and Ni^{II} (Table I) in itself also provides

Table I. Five-Coordinate Complexes from Trimethylphosphine Oxide and Trimethylarsine Oxide

$[Mn(Me_3PO)_5](ClO_4)_2$	[a]	$[Co(Me_3PO)_5](ClO_4)_2$ [b]	$[Ni(Me_3PO)_5](ClO_4)_2$	[a]
$[Mn(Me_3AsO)_5](ClO_4)_2$	[a]	$[Co(Me_3AsO)_5](ClO_4)_2$ [b]	$[Ni(Me_3AsO)_5](ClO_4)_2$ [c]	[a]
	$[Fe(Me_3PO)_4(ClO_4)]ClO_4$	[a]		$[Cu(Me_3PO)_4(ClO_4)]ClO_4$
$[Mn(Me_3AsO)_4(ClO_4)]ClO_4$	$[Fe(Me_3AsO)_4(ClO_4)]ClO_4$	[a]	$[Ni(Me_3AsO)_4(ClO_4)]ClO_4$	$[Cu(Me_3AsO)_4(ClO_4)]ClO_4$ [d]
	$[Fe(Me_3AsO)_4(ClO_4)]BPh_4$		$[Ni(Me_3AsO)_4(ClO_4)]BPh_4$	

[a] Complexes could not be isolated. [b] With these ligands cobalt also forms tetrahedral complexes $[CoL_4](ClO_4)_2$, isomorphous with their zinc analogues (refs. 5 and 6). [c] Corresponding compounds $[Ni(Me_3AsO)_5]X_2$, with $X = NO_3^-$ or BF_4^- were obtained. [d] A tetraphenylborate analogue could not be prepared.

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Table II. Band Maxima (kK) for Diffuse Reflectance Spectra

$[Fe(Me_3PO)_4(ClO_4)]ClO_4$	9.8 w br
$[Fe(Me_3AsO)_4(ClO_4)]ClO_4$	11.0 w br
$[Co(Me_3PO)_5](ClO_4)_2$	20.2 sh, 19.65 s, 18.4 s, 16.9 s, 10.5 m, 7.6 m br
$[Co(Me_3AsO)_5](ClO_4)_2$	19.6 s, 18.7 s, 17.0 s, 11.0 m, 8.5 m br
$[Ni(Me_3PO)_5](ClO_4)_2$	22.2 s, 19.4 sh, 17.3 w, 13.95 w, 10.8 m, 8.3 w br [a]
$[Ni(Me_3AsO)_5](ClO_4)_2$	22.2 s, 19.2 m, 17.15 w, 13.6 sh, 11.3 m, 8.6 w br [a]
	22.2 (120), 19.2 sh, 17.2 sh, 13.6 (5), 11.3 (20), 8.6 sh [b]
$[Ni(Me_3AsO)_5](BF_4)_2$	22.1 s, 19.1 m, 17.15 w, 13.5 sh, 11.3 m, 8.7 w br [a]
$[Ni(Me_3AsO)_5](NO_3)_2$	22.2 s, 19.1 m, 17.15 w, 13.55 sh, 11.3 m, 8.6 w br [a]
$[Ni(Me_3AsO)_4(ClO_4)]ClO_4$	22.3 s, 19.4 m, 17.2 sh, 15.6 w, 13.5 sh, 11.2 m, 8.6 w br [a]
$[Ni(Me_3AsO)_4(ClO_4)](BPh_4)$	22.3 s, 19.4 sh, 17.2 sh, 15.4 w, 13.4 sh, 11.3 m, 8.6 w br [a]
$[Cu(Me_3PO)_4(ClO_4)]ClO_4$	16.7 sh, 11.4 m br
$[Cu(Me_3AsO)_4(ClO_4)]ClO_4$	17.0 sh, 14.5 m br
$[Co(Me_3PO)_5(H_2O)](ClO_4)_2$ [c]	20.5 sh, 18.45 m, 13.25 w, 8.5 mw, 7.0 m
$[Co(Me_3PO)_4(H_2O)_2](ClO_4)_2$ [c]	20.5 sh, 18.45 m, 13.25 w, 10.0 mw, 8.5 mw, 7.0 mw
$[Ni(Me_3PO)_5(H_2O)](ClO_4)_2$ [c]	23.2 m, 14.5 sh, 12.2 m, 7.1 m br
$[Ni(Me_3AsO)_4(NO_3)](BPh_4)$ [c]	23.4 m, 13.7 sh, 12.3 m, 7.2 w br

[a] For the five-coordinate nickel complexes there is also evidence of a band with maximum below 5kK. [b] Acetone solution (2.16×10^{-3} *M*), with molar extinction coefficients in parentheses. [c] Octahedral complex.

evidence for this formulation. The copper compounds of composition $CuL_4(ClO_4)_2$, L=Me_3PO and Me_3AsO, give similar powder photographs to those from the other $[ML_4(ClO_4)]^+$ complexes (though with several additional lines in the case of the arsine oxide complex). They are therefore considered to have essentially the same configuration. A square planar structure has previously been assigned[4] to the complex of composition $Cu(Me_3PO)_4(ClO_4)_2$. With zinc only $[ZnL_4]^{2+}$ complexes, isomorphous with their tetrahedral cobalt analogues, could be isolated.[5,6] However, a lowering of the ν(M–O) mode from 430 cm^{-1} to about 400 cm^{-1} when excess ligand was added to a nitromethane solution of $[Zn(Me_3AsO)_4](ClO_4)_2$ may be taken as indication of the development of higher coordination (see below). It is of interest that crystalline five-coordinate $[ZnL_5]^{2+}$ and $[ZnL_4(ClO_4)]^+$ complexes can be obtained with the related diphenylmethylphosphine oxide and arsine oxide.[6,7]

Somewhat surprisingly the ν(Cl–O) absorptions do not give definite indication of perchlorate coordination for the $[ML_4(ClO_4)]^+$ complexes. There is no conspicuous splitting of the ν(Cl–O) band as is usually observed for anion coordination[8] although a shoulder appears at 1065 cm^{-1} for the BPh_4^- complexes. However, it is recognised that this is not a reliable criterion and anion coordination (ClO_4^- and BF_4^-) has been established for a number of compounds which do not show splitting of anion absorptions.[9,10,11] On the other hand correlations of the degree of splitting and the strength of coordination have been made[9] and on this basis the lack of splitting for these complexes indicates a weak association of perchlorate.

With the ligands Ph_2MePO and Ph_2MeAsO complexes of the $[ML_4(ClO_4)]^+$ type (M=Mn, Co, Ni, and Zn) do by contrast show considerable splitting of ν(Cl–O) absorptions,[6,7] indicating stronger perchlorate coordination. From a steric point of view it is unlikely that the diphenylmethyl substituents provide a significantly more favourable arrangement for perchlorate coordination than the trimethyl analogues although the smaller steric requirement of trigonal than tetrahedral carbon may be helpful. In fact a limited examination has shown that with Ph_2MePO, $[ML_5]^{2+}$ compounds of iron, cobalt, nickel, and zinc can also be isolated[6] and this shows that the diphenylmethyl ligands are certainly not less favourable for the formation of five-coordinate complexes.

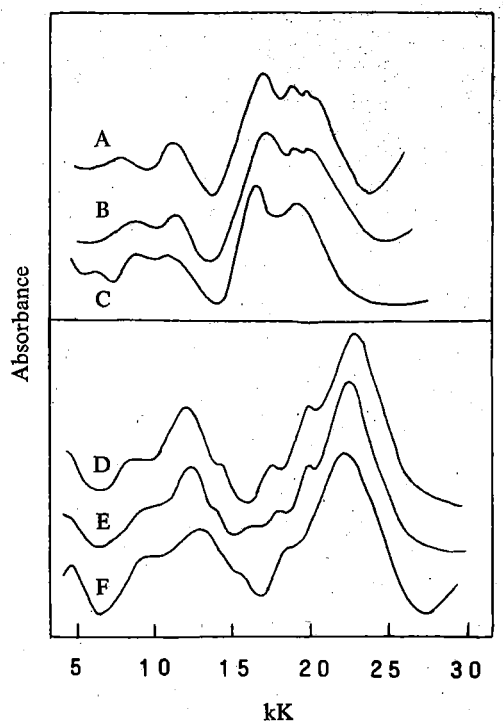

Figure 1. Electronic Reflectance Spectra: A, $[Co(Me_3PO)_5](ClO_4)_2$; B, $[Co(Me_3AsO)_5](ClO_4)_2$; C, $[Co(Me_5dien)Cl_2]$; D, $[Ni(Me_3AsO)_5](ClO_4)_2$; E, $[Ni(Me_3AsO)_4(ClO_4)]ClO_4$; F, $[Ni(Me_5dien)Cl_2]$.

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Table III. Infrared Spectra (cm^{-1})

Compound	ν(P—O), ν(As—O)	ν(M—O)	Other bands (500-200 cm^{-1})
Me_3PO	1166 s	—	375 sh, 365 m, 315 w, 242 vw
$[Mn(Me_3PO)_5](ClO_4)_2$	1146 s, 1135 s	404 m, 400 m	363 m, 320 w, 255 vw
$[Fe(Me_3PO)_4(ClO_4)]ClO_4$	[a]	423 m	366 m, 265 vw, 242 vw
$[Co(Me_3PO)_5](ClO_4)_2$	1145 s	409 m	365 m, 324 w, 258 vw
$[Ni(Me_3PO)_5](ClO_4)_2$	1141 s, 1132 s	420 m	366 m, 324 w, 258 vw
$[Cu(Me_3PO)_4(ClO_4)]ClO_4$	1120 sh	466 m, 454 m	363 m, 338 w, 261 vw
Me_3AsO	870 s	—	266 m
$[Mn(Me_3AsO)_5](ClO_4)_2$	869 s, 863 s	366 m	284 m
$[Mn(Me_3AsO)_4(ClO_4)]ClO_4$	868 s, 855 sh	368 m, br	306 w, 279 m
$[Fe(Me_3AsO)_4(ClO_4)]ClO_4$	861 s	402 m, br	307 m, 283 sh
$[Fe(Me_3AsO)_4(ClO_4)]BPh_4$	855 s	415 m, br	468 w,[b] 300 m, 279 m
$[Co(Me_3AsO)_5](ClO_4)_2$	867 s, 857 sh	407 m, 391 m	285 m
$[Ni(Me_3AsO)_5](ClO_4)_2$	866 s	407 m	290 m
$[Ni(Me_3AsO)_5](BF_4)_2$	866 s	407 m	291 m, 278 sh
$[Ni(Me_3AsO)_5](NO_3)_2$	866 s	408 m	290 m, 279 sh
$[Ni(Me_3AsO)_4(ClO_4)]ClO_4$	866 s	407 m, br	283 m
$[Ni(Me_3AsO)_4(ClO_4)]BPh_4$	864 s	410 m, br	468 w,[b] 293 m, 280 sh
$[Cu(Me_3AsO)_4(ClO_4)]ClO_4$	854 m, 833 s[c]	470 m	288 m, 268 sh

[a] Obscured by perchlorate band. [b] BPh_4^- band. [c] Contains methyl rocking mode normally observed at 840 cm^{-1}.

The infrared data are presented in Table III. The ν(P—O) and ν(As—O) modes are affected by coordination in the usual manner. The simplicity of the ligand spectra enabled additional bands for the complexes to be assigned as ν(M—O) modes. Only one such band was usually observed for each complex, although three would be expected for square pyramidal ML_5 structures[12] and an identifiable perchlorate ν(M—O) absorption for the $[ML_4(ClO_4)]^+$ complexes might be anticipated. It is significant that lower ν(M—O) values arise from the five-coordinate cobalt complexes as compared with values for the four-coordinate tetrahedral complexes (460,448 cm^{-1} for $[Co(Me_3PO)_4](ClO_4)_2$; 442,428 cm^{-1} for $[Co(Me_3AsO)_4](ClO_4)_2$).[5,13] Assuming the generality of this effect it may be used to distinguish between four- and five-fold coordination as mentioned above for zinc complexes. As has been generally observed for other oxo complexes low ν(M—O) values are found for manganese complexes and high values for copper.[14]

The magnetic moments show that all the complexes are of the high-spin type, the values lying within the ranges observed for other high-spin five-coordinate complexes. Those found for the nickel compounds (3.56-3.63 B.M.) are such as to exclude the possibility of octahedral coordination (range 2.9-3.3 B.M.).

From the wide range of complexes with oxo ligands now available it appears that the $[ML_5]^{2+}$ compounds are the first examples of five-fold coordination with identical oxo ligands. Edwards *et al.*[15] have studied oxo complexes in relation to coordination number and although a complex of composition $Cd(Me_2SO)_5(ClO_4)_2$ is reported no evidence for five-coordination, beyond the elemental analysis, is presented. The trimethylphosphine and arsine oxides are apparently sufficiently small to enable five-fold coordination but bulky enough to prevent six-coordination as found for other «smaller» oxo ligands such as pyridine-N-oxide[16] and dimethylsulphoxide.[17] This is further indicated by the fact that the spectrum of the one complex which was sufficiently stable to study in solution, $[Ni(Me_3AsO)_5](ClO_4)_2$, was unaffected by excess ligand.

While ML_6 complexes could not be obtained with the Me_3XO ligands (X=P or As) an isomorphous series of six-coordinate $[M(Me_3PO)_5(H_2O)](ClO_4)_2$ derivatives (M=Mn, Co, and Ni) was obtained upon exposure of the $[M(Me_3PO)_5](ClO_4)_2$ compounds to atmospheric moisture, indicating that a sufficiently small ligand can increase the coordination to six. That only the Me_3PO complexes show this behaviour may be associated with the lower steric requirement of the phosphine oxide than the arsine oxide, although a higher electrophilicity of the metal atom (due to a smaller net charge transfer by the weaker Me_3PO donor[13]) may be an important factor. The tetrahedral complex $[Co(Me_3PO)_4](ClO_4)_2$ is also much more sensitive to moisture than its arsine oxide analogue, giving a six-coordinate dihydrate $[Co(Me_3PO)_4(H_2O)_2](ClO_4)_2$ (Table II). It is of interest however that trimethylarsine oxide in association with a small bidentate nitrate ligand does form a six-coordinate complex $[Ni(Me_3AsO)_4(NO_3)]BPh_4$. The electronic spectum of this compound (Table II), characteristic of an octahedral complex, excludes the possibility of five-coordination (as found for the perchlorate $[Ni(Me_3AsO)_4ClO_4]BPh_4$) and establishes the bidentate role of the nitrate.

In view of its similar shape to the phosphine and arsine oxides trimethylamine oxide might also be expected to form five-coordinate complexes, but isolation of such compounds did not prove possible. The amine oxide usually gives four-coordinate complexes, but its ability to develop six-coordination, as in $[Cr(Me_3NO)_6](ClO_4)_3$,[18] indicates that an

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$[M(Me_3NO)_5]$ species might not be stabilised by steric interactions as was postulated for the trimethylphosphine and arsine oxide ligands. Although the addition of excess ligand to $[Co(Me_3NO)_4]^{2+}$ and $[Ni(Me_3NO)_4]^{2+}$ in nitromethane produces spectral changes indicating the attainment of a higher coordination than four, crystalline complexes could not be isolated from these solutions. Likewise it was not possible to isolate five-coordinate complexes with hexamethylphosphoramide which, like Me_3NO, produces both four- and six-coordinate compounds.[19]

Experimental Section

Preparation of Complexes. The $[ML_5]X_2$ complexes ($L=Me_3PO$, Me_3AsO; $X=ClO_4^-$, BF_4^-, NO_3^-) were obtained from reaction of the metal salt in anhydrous acetone with a slight excess of ligand. In the preparation of $[Ni(Me_3AsO)_5](ClO_4)_2$, for example, hydrated nickel perchlorate (0.22 g) in hot acetone (10 ml) containing ethyl orthoformate (1 ml) as dehydrating agent was added to the arsine oxide (0.42 g) in the same solvent. Orange crystals separated on cooling. As standard procedure the product was washed successively with solvent and ether, and dried under high vacuum. The $[ML_4(ClO_4)]ClO_4$ derivatives, on the other hand, separated from hot anhydrous ethanol (with ethyl orthoformate) following the addition of ligand (4 moles) to the metal perchlorate (1 mole). All samples were handled in a dry box, though this was not strictly necessary for the $[M(Me_3AsO)_5]^{2+}$ compounds whose reaction with atmospheric moisture was slow. Infrared spectra were examined routinely to confirm absence of water. It was checked by direct weighing that uptake of water by $[Co(Me_3PO)_5](ClO_4)_2$ and $[Co(Me_3PO)_4](ClO_4)_2$ corresponded to 1 and 2 moles respectively. The arsine oxide complexes of manganese are susceptible to atmospheric oxidation. They were therefore prepared and stored under nitrogen. Attempts to prepare $[ML_5]^{2+}$ complexes of iron, copper, and zinc using different solvents, temperatures, and conditions of crystallisation were unsuccessful.

In the preparation of $[Ni(Me_3AsO)_4(ClO_4)]BPh_4$ sodium tetraphenylborate (0.149 g) and arsine oxide (0.426 g) in hot anhydrous ethanol (15 ml) were added to hydrated nickel perchlorate (0.164 g) in hot ethanol (10 ml) with ethyl orthoformate. For the iron compound excess sodium tetraphenylborate was required.

Analyses are given in Table IV. With $[Ni(Me_3PO)_5](ClO_4)_2$ which was particularly sensitive to uptake of moisture figures are given for the derived monohydrate.

The manganese compounds from both the phosphine and arsine oxides are white, the iron are buff, cobalt mauve, nickel $[NiL_5]^{2+}$ orange, nickel $[NiL_4(ClO_4)]^{2+}$ yellow, and copper pale blue. When dissolved in nitromethane the cobalt complexes $[CoL_5]^{2+}$ reverted to blue $[CoL_4]^{2+}$ derivatives. The analogous nickel compounds are more resistant to decomposition. The absorption spectrum of $[Ni(Me_3AsO)_5](ClO_4)_2$ in acetone, though showing some deviation from Beer's law, is essentially the same as that of the solid. The compound is a 2:1 electrolyte in this solvent. In nitromethane the compound shows spectral changes probably associated with partial development of octahedral coordination. The $[NiL_4(ClO_4)]^+$ compounds suffer more complete decomposition in solution and behave as 2:1 electrolytes.

Table IV. Analyses

Compound	Found %		Calculated %	
	C	H	C	H
$[Mn(Me_3PO)_5](ClO_4)_2$	25.0	6.2	25.2	6.3
$[Co(Me_3PO)_5](ClO_4)_2$	25.1	6.1	25.1	6.3
$[Ni(Me_3PO)_5(H_2O)](ClO_4)_2$	24.3	6.4	24.4	6.4
$[Fe(Me_3PO)_4(ClO_4)]ClO_4$	22.2	5.8	23.1	5.8
$[Cu(Me_3PO)_4(ClO_4)]ClO_4$	23.0	6.1	22.8	5.7
$[Mn(Me_3AsO)_5](ClO_4)_2$	19.3	4.8	19.3	4.8
$[Mn(Me_3AsO)_4(ClO_4)]ClO_4$	18.2	4.6	18.1	4.5
$[Fe(Me_3AsO)_4(ClO_4)]ClO_4$ [a]	17.5	4.6	18.0	4.5
$[Co(Me_3AsO)_5](ClO_4)_2$ [b]	19.4	4.9	19.2	4.8
$[Ni(Me_3AsO)_5](ClO_4)_2$ [c]	19.15	4.8	19.2	4.8
$[Ni(Me_3AsO)_5](BF_4)_2$	20.0	5.4	19.7	4.9
$[Ni(Me_3AsO)_5](NO_3)_2$	20.5	5.8	20.9	5.2
$[Ni(Me_3AsO)_4(ClO_4)]ClO_4$ [d]	18.0	4.6	18.0	4.5
$[Ni(Me_3AsO)_4(ClO_4)]BPh_4$	43.0	5.6	42.3	5.5
$[Ni(Me_3AsO)_4(NO_3)]BPh_4$	45.0	5.8	43.9	5.7
$[Cu(Me_3AsO)_4(ClO_4)]ClO_4$	17.9	4.7	17.9	4.5

[a] Fe, 7.3%; (calcd. 7.0). [b] Co, 5.9 (6.3). [c] Ni, 6.3 (6.3). [d] Ni, 7.6 (7.3).

Physical Measurements. Electronic spectra were run over the range 5-30 kK using a Beckman DK2A spectrophotometer with standard reflectance attachment for solid samples. Infrared spectra were obtained from nujol mulls using Perkin Elmer 337 (to 400 cm^{-1}) and Grubb Parsons DM4 (500-200 cm^{-1}) spectrophotometers. Calibrations were made with polystyrene and water vapour respectively.

Electrolytic conductivities were measured in anhydrous nitromethane at concentrations close to 10^{-3} *M*. Magnetic susceptibility measurements were made by the Gouy method at room temperature, using $[Nien_3]S_2O_3$ as calibrant.[20] Diamagnetic corrections from Pascal constants were made. Values (B.M.) obtained for trimethylarsine oxide complexes were: $[MnL_5](ClO_4)_2$, 6.05; $[FeL_4(ClO_4)]ClO_4$, 4.94; $[CoL_5](ClO_4)_2$, 4.80; $[NiL_5](ClO_4)_2$, 3.62; $[NiL_5](BF_4)_2$, 3.63; $[NiL_4(ClO_4)]ClO_4$, 3.56; $[CuL_4(ClO_4)]ClO_4$, 2.02.

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Inorg. Phys. Theor.—8/420—1

Cobalt(II) Complexes with Trimethylphosphine Oxide and Trimethylphosphine Sulphide

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The preparation of new tertiary phosphine sulphide and arsine sulphide complexes of cobalt(II) is reported and comparative spectral and magnetic data presented for Me_3PO and Me_3PS tetrahedral complexes of the types $[CoL_4](ClO_4)_2$ and CoL_2X_2 (X = Cl, Br, and I). The results demonstrate the high metal-ligand covalency which is produced by thioxo-ligands. Electronic spectra for complexes with Me_3PO, MePS, and related ligands are compared. A conspicuous feature of the spectra of $[CoL_4]^{2+}$ complexes with oxo-ligands is that phosphine oxides produce an identical ν_3 band profile while arsine oxides produce a different, characteristic profile. By contrast, phosphine and arsine sulphides do not produce marked differences in the splitting of electronic bands.

ALTHOUGH there are numerous examples in the literature of tertiary phosphine and arsine sulphides forming complexes with 'class b' acceptors, examples with 'class a' acceptors are less common.[1] Recently it was found that trimethylarsine sulphide reacts readily with iron(II), cobalt(II), and nickel(II).[2] This prompted a closer examination of the co-ordinating properties of trimethylphosphine, triphenylarsine, and triphenylphosphine sulphides. In contrast to earlier reports [1] it was found that a full range of Co^{II} complexes could be obtained with trimethylphosphine sulphide and also that triphenylarsine sulphide reacted with cobalt(II) salts, although in the latter case only impure products were obtained. There was no definite indication of complex formation for triphenylphosphine sulphide with cobalt(II).

This report deals primarily with spectroscopic and magnetic data for trimethylphosphine sulphide and oxide complexes which complement data reported earlier for complexes of the arsenic analogues (Me_3AsS and Me_3AsO).[2] *X*-Ray powder photographs show that cobalt(II) complexes with trimethylphosphine oxide and trimethylphosphine sulphide are respectively isostructural with their arsenic analogues. Moreover the photographs of related halide complexes with the phosphine oxide and sulphide are themselves similar, as was found for the corresponding arsenic compounds.[2] The essentially tetrahedral structure for the cobalt(II) complexes of trimethylphosphine oxide and sulphide is apparent from their electronic spectra (Table 1).

Relationships between both the spectral parameters and the magnetic properties of the phosphine oxide and sulphide complexes closely parallel those found between their arsenic analogues.[2] Thus, the close similarity of the ligand-field splitting energies, Δ, for the perchlorate complexes, $[Co(Me_3PO)_4](ClO_4)_2$ and $[Co(Me_3PS)_4]ClO_4)_2$, again enables differences in magnetic moments to be interpreted primarily in terms of spin–orbit coupling. The magnetic moment of the compound $[Co(Me_3PS)_4](ClO_4)_2$

TABLE 1

Electronic spectral data for cobalt(II) complexes ($cm.^{-1}$) [a]

Compound	State								
$[Co(M_3PO)_4](ClO_4)_2$	$PhNO_2$	18,250(152)	17,990(154)	17,120(221)	16,690(223)	15,920(242)	7410(34)	6540(36)	5850(33)
	Solid		18,180(sh,br)		16,670	16,000	7580	6760	5880
$Co(Me_3PO)_2Cl_2$	CH_2Cl_2	16,750(260)	16,160(sh)	15,600(389)	15,060(449)		6990(53)	5850(50)	
	Solid	16,750	16,260	15,800	14,880		6940	5850	
$Co(Me_3PO)_2Br_2$	CH_2Cl_2	16,720(sh)	16,030(360)	15,460(433)	14,680(456)		6710(64)	5750(60)	
	Solid	16,950	16,580	15,620	14,140		6670	5680	
$Co(Me_3PO)_2I_2$.....	CH_2Cl_2	16,260(427)	15,770(sh)	15,200(490)	13,950(422)		6370(94)	5590(90)	
	Solid	16,260		15,040	13,850		6330	5460	
$[Co(Me_3PS)_4](ClO_4)_2$	$PhNO_2$ [b]	15,380(526)	14,490(705)	13,510(650)			7350(143)	6000(143)	
	Solid	15,400	14,800	13,600			7350	5950	
$Co(Me_3PS)_2Cl_2$	$PhNO_2$	16,560(436)	15,170(436)	13,330(457)			6900(sh)	5210(123)	
	Solid	16,100	14,800	13,600			6600	5250	
$Co(Me_3PS)_2Br_2$	CH_2Cl_2	15,850(468)	14,730(506)	13,230(540)			6620(sh)	5000(115)	
	Solid	15,600	14,200	13,500			6500	4900	
$Co(Me_3PS)_2I_2$	CH_2Cl_2	14,840(575)	13,870(749)	12,820(871)			6350(117)	4940(117)	
	Solid	14,800	13,700	12,800			6100	4800	
$[Co(Ph_3AsS)_4](ClO_4)_2$	$PhNO_2$ [b]	15,150	14,370	13,890			7840	5920	
	Solid	15,100	14,350	13,900			7800	5900	
$Co(Ph_3AsS)_2Br_2$.....	CH_2Cl_2 [b]	15,820	14,470	13,090			6600(sh)	4960	
	Solid	15,700	14,600	13,300			6600	4700	

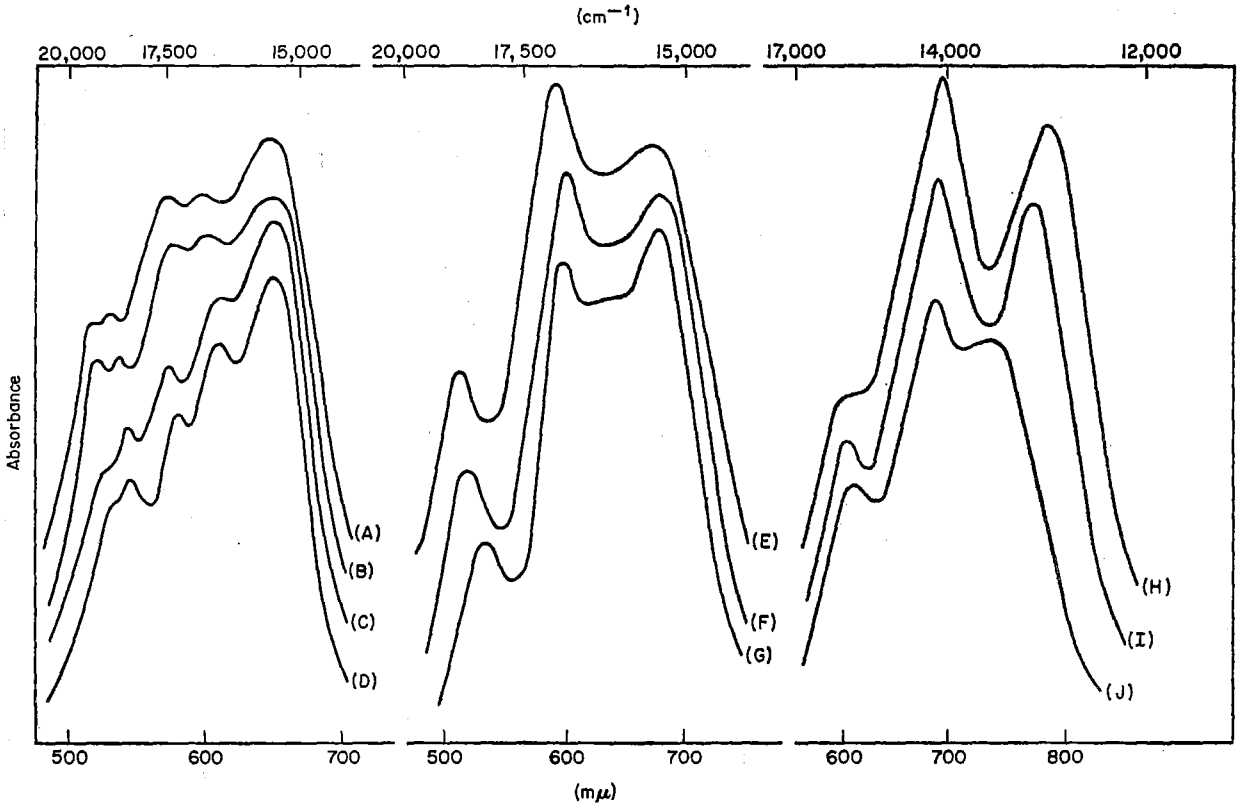
[a] Molar extinction coefficients in parentheses. [b] Plus excess ligand.

TABLE 3

I.r. spectra (600—200 $cm.^{-1}$) [a]

	ν(P–S), ν(As–S)	ν(Co–S), ν(Co–O)	ν(Co–X)	ν(ligand)
Me_3PS	565s			280vw, 225vw
$[Co(Me_3PS)_4](ClO_4)_2$	538sh, 530s, 525sh	330m, 321m [b]		290vw, 260vw, 225vw
$Co(Me_3PS)_2Cl_2$	538sh, 533s	(325sh, 320s, 308s, 282m) [c]		255vw
$Co(Me_3PS)_2Br_2$	536s	316m, 310m	246sh, 240s	275vw, 258w
$Co(Me_3PS)_2I_2$	531s	317m, 311m		275vw, 257w
Ph_3AsS	495s			474m, 467m, 457w, 345m, 326m, 297vw
$[Co(Ph_3AsS)_4](ClO_4)_2$	[e]	282m, 275m		475m, 464s, 455sh, 441sh, 345s, 330sh, 297vw
$Co(Ph_3AsS)_2Br_2$.....	[e]	(260sh, 250m, 245m) [d]		469s, 444m, 348s, 343s, 298vw
$[Zn(Ph_3AsS)_4](ClO_4)_2$	[e]	275m		477m, 465s, 455sh, 446sh, 346s, 337sh
Me_3PO [f]				375sh, 365m, 315w, 242vw
$[Co(Me_3PO)_4](ClO_4)_2$		460sh, 448m [g]		352m, 328w, 255vw

[a] For Nujol mulls. [b] Values of ν(Co–S) for nitromethane solution are 330m, 323sh. [c] ν(Co–S) + ν(Co–Cl). [d] ν(Co–S) + ν(Co–Br). [e] For the complexes ν(As–S) is indistinguishable from other ligand bands. [f] For $(Me_3PO)_2X_2$ complexes see ref. 11. [g] For solution spectrum nitromethane band interferes with ν(Co–O).



ν_3 Band profiles for solution spectra of groups of $[CoL_4]^{2+}$ species: (A) L = Me_3PO, (B) Ph_2MePO, (C) $(NMe_2)_3PO$, (D) Ph_3PO, (E) Me_3AsO, (F) Ph_2MeAsO, (G) Ph_3AsO, (H) Me_3AsS, (I) Me_3PS, (J) Ph_3AsS

is *ca.* 0·25 B.M. lower than that for $[Co(Me_3PO)_4](ClO_4)_2$. This is a very similar situation to that found for the arsenic analogues and substantiates our earlier conclusion [2] that a lower magnetic moment for a thioxo-ligand arises primarily from decreased spin–orbit coupling which in turn can be related to increased metal-ligand covalency. Again, the sulphide complexes $[Co(Me_3PS)_4](ClO_4)_2$ and $Co(Me_3PS)_2X_2$ (X = Cl, Br, or I) have considerably lower β values and higher oscillator strengths for their electronic absorptions than those for the corresponding oxo-complexes (Table 2), further establishing the greater metal-ligand covalency attained by thioxo-ligands.

TABLE 2

Electronic Spectral Parameters

Compound	ν_3 (cm.$^{-1}$)[a]	ν_2 (cm.$^{-1}$)[a]	Δ (cm.$^{-1}$)[b]	β[c]	f(ν_3) (× 10^3)[d]
$[Co(Me_3PO)_4](ClO_4)_2$	16,890	6600	3800	0·83	3·22
$Co(Me_3PO)_2Cl_2$	15,750	6440	3730	0·76	4·54
$Co(Me_3PO)_2Br_2$	15,590	6230	3590	0·76	4·63
$Co(Me_3PO)_2I_2$	15,300	6000	3450	0·75	6·28
$[Co(Me_3PS)_4](ClO_4)_2$	14,400	6680	3890	0·65	8·59
$Co(Me_3PS)_2Cl_2$	14,990	5810	3340	0·74	6·80
$Co(Me_3PS)_2Br_2$	14·540	5700	3280	0·72	7·42
$Co(Me_3PS)_2I_2$	13,710	5650	3260	0·66	9·18
$[Co(Ph_3AsS)_4](ClO_4)_2$	14,430	6940	4060	0·63	
$Co(Ph_3AsS)_2Br_2$	14,510	5600	3220	0·72	
$[Co(Me_3AsO)_4](ClO_4)_2$[e]	16,810	6900	3980	0·81	3·78
$[Co(Me_3AsS)_4](ClO_4)_2$[e]	14,280	6950	4070	0·62	9·62

[a] Evaluated from the centre of gravity of the intensities. [b] Calculated by the methods described in ref. 3; considered reliable to ±100 cm.$^{-1}$. [c] β = B (complex)/967; reliable to ±0·01. [d] Oscillator strength, *f*, evaluated graphically. [e] From ref. 1; included for comparison with other data.

The present results together with those reported earlier for trimethylarsine oxide and trimethylarsine sulphide complexes [2] also provide information on the differing effects of phosphorus and arsenic on the bonding of oxo- and thioxo-ligands. Both the phosphine oxide and sulphide produce lower crystal-field splitting energies, Δ, than their arsenic analogues. Trimethylphosphine oxide is a considerably weaker base than the arsine oxide [4] and other data for these ligands (*e.g.* $J(C^{13}\text{-H})$ coupling constants,[5,6] and the estimated P–O and As–O force constants [7,8]) indicate a greater degree of oxo-π-bonding in the P–O linkage. This would lead to weaker donor power and hence lower Δ values for phosphine oxide. In view of the uncertainty about the extent of π-bonding in thioxo-ligands,[9,10] it is not possible to discuss the effect of this on Δ values. Also, differences in polarisabilities are likely to be more important for thioxo-ligands. Too much emphasis should not be placed on the relatively small differences in Δ, particularly in view of the difficulties in deriving reliable Δ values for Co^{II} tetrahedral complexes.[11] However, it is noteworthy that Δ values are consistently higher for CoL_2X_2 complexes with L = Me_3AsO or Me_3AsS compared respectively with their phosphorus analogues, paralleling the situation for the $[CoL_4]^{2+}$ species.

A further indication of the influence of the penultimate atom on the bonding of these ligands may be obtained from details of the ν_3 band profiles. Although the positions of the ν_3 bands for $[Co(Me_3PO)_4](ClO_4)_2$ and the isostructural complex $[Co(Me_3AsO)_4](ClO_4)_2$ are similar, their profiles (Figure) are quite different. The difference in the band splitting does not appear to be a function of Δ because other oxo-ligands, which produce different Δ values, follow a similar pattern. Thus, Ph_3PO, Ph_2MePO, and $(Me_2N)_3PO$ have virtually the same band profile (Figure) as that observed for Me_3PO, while profiles for Ph_3AsO and Ph_2MeAsO parallel closely that for Me_3AsO. A likely explanation is that basic differences in M–O bonding for phosphine oxide and arsine oxide ligands, arising from differences in d_π–p_π bonding, produce slightly different spacings between components of the ^4P and ^2G states, which in turn would lead to different spin–orbit coupling and consequently different band profiles. By contrast the thioxo-ligands do not produce marked differences in the ν_3 band profiles for $[CoL_4]^{2+}$ complexes. The bands are virtually identical for trimethylphosphine sulphide and trimethylarsine sulphide derivatives while the spectrum for the triphenylarsine sulphide complex is similar (Figure). This indicates that Co–S interactions are not affected by the penultimate atom (*i.e.* P or As) as appears to be the case for Co–O oxo-bonding, which may imply that π-bonding (P–S and As–S) is less important for thioxo-ligands.

The $\nu_2[^4A_2 \longrightarrow {}^4T_1(F)]$ absorption bands also differ for $[CoL_4]^{2+}$ oxo- and thioxo-complexes. In the former case three main bands are invariably found while in the latter only two components appear. Unlike the ν_3 band, there is no apparent difference between profiles for phosphine oxide and arsine oxide complexes. This further indicates that the different features observed for ν_3 are primarily related to different interactions between excited quartet and adjacent doublet states. The effects of lower symmetry are more apparent for the ν_2 transition [11] and the observed differences for oxo- and thioxo-complexes many indicate less distortion in the latter case, as might be expected for the larger sulphur donor atom. However, splitting of ν(Co–O) and ν(Co–S) i.r. bands in $[CoL_4](ClO_4)_2$ complexes, L = Me_3PO, Me_3AsO, Me_3PS, and Me_3AsS, indicates that the point symmetry is lower than T_d in all cases. Results for the Me_3PO and Me_3PS complexes are given in Table 3. For $[Co(Me_3AsS)_4](ClO_4)_2$, ν(Co–S) is split in nitromethane solution (312 and 295 cm.$^{-1}$) as was observed for the solid state.[2] Also, in the case of the corresponding oxo-complex ν(Co–O) is split in the solid state [2] and broad in solution. Low frequency results for $Co(Me_3PS)_2X_2$ (X = Cl, Br, I) and the Ph_3AsS complexes are included in Table 3, while data for $Co(Me_3PO)_2X_2$ complexes (X = Cl, Br, or I) are reported elsewhere.[12]

EXPERIMENTAL

Preparations and Analyses.—Trimethylphosphine sulphide (m.p. 155—156°) and triphenylarsine sulphide (m.p. 163°) were prepared by published methods.[13,14] The phosphine sulphide complexes were obtained from the ligand and cobalt salt in hot anhydrous ethanol, preferably with addition of ethyl orthoformate.[15] The products, which crystallized on cooling, were washed with ethanol and ether,

and dried *in vacuo*. Of the phosphine oxide derivatives the halides $Co(Me_3PO)_2X_2$ have been described previously.[12] The perchlorate $[Co(Me_3PO)_4](ClO_4)_2$, prepared as above, is extremely hygroscopic, being converted reversibly to a pink hydrate. Manipulations were therefore made under moisture-free conditions. The magnetic moment was reproducible for different samples. The i.r. spectrum reported previously [16] corresponds with that of the hydrate.

In preparing the triphenylarsine sulphide complexes the hot ethanol solutions containing ethyl orthoformate were evaporated until viscous. Upon cooling the solution and adding ether crystals were obtained, but the products were contaminated with unchanged reactants. These could not be eliminated by recrystallisation, use of different solvents, or different reactant ratios. The perchlorate complex was identified as $[Co(Ph_3AsS)_4](ClO_4)_2$ from its isomorphism with the pure zinc analogue.

The *compounds* gave the following analyses: $[Co(Me_3PO)_4](ClO_4)_2$ (Found: C, 23·6; H, 5·7; Co, 9·4. $C_{12}H_{36}Cl_2CoO_{12}P_4$ requires C, 23·0; H, 5·75; Co, 9·4%). $[Co(Me_3PS)_4](ClO_4)_2$ (Found: C, 21·1; H, 5·1; Co, 8·3. $C_{12}H_{36}Cl_2CoO_8P_4S_4$ requires C, 20·9; H, 5·2; Co, 8·5%). $Co(Me_3PS)_2Cl_2$ (Found: C, 20·9; H, 5·2; Cl, 20·0. $C_6H_{18}Cl_2CoP_2S_2$ requires C, 20·8; H, 5·2; Cl, 20·5%). $Co(Me_3PS)_2Br_2$ (Found: C, 16·7; H, 4·2; Br, 36·6. $C_6H_{18}Br_2CoP_2S_2$ requires C, 16·6; H, 4·1; Br, 36·7%). $Co(Me_3PS)_2I_2$ (Found: C, 13·9; H, 3·4; Co, 10·8. $C_6H_{18}CoI_2P_2S_2$ requires C, 13·6; H, 3·4; Co, 11·1%). $Co(Ph_3AsS)_2Br_2$ (Found: C, 46·4; H, 3·5. $C_{36}H_{30}As_2Br_2CoS_2$ requires C, 48·3; H, 3·35%). $[Zn(Ph_3AsS)_4](ClO_4)_2$ (Found: C, 53·0; H, 3·9. $C_{72}H_{60}As_4Cl_2O_8S_4Zn$ requires C, 53·4, H, 3·7%).

Physical Measurements.—These were made as described previously.[2] In recording the electronic spectra of the relatively unstable complexes $[Co(Me_3PS)_4](ClO_4)_2$, $[Co(Ph_3AsS)_4](ClO_4)_2$ and $Co(Ph_3AsS)_2Br_2$ which show ligand dissociation in nitromethane solution, free ligand was added to restore band intensities to their maximum values. Spectra of the ions $[CoL_4]^{2+}$ (L = Ph_2MeAsO and Ph_2MePO) were obtained from solutions of the perchlorates $[CoL_4(ClO_4)]ClO_4$ in nitromethane. These compounds are five-co-ordinate in the crystalline state,[6,17] but give tetrahedral spectra in solution. The solution spectrum of $[Co(Ph_3AsO)_4](ClO_4)_2$ was also recorded on a Cary 14 Spectrophotometer in view of a minor discrepancy with a previously reported spectrum.[18]

Magnetic moments were corrected for diamagnetism and temperature independent paramagnetism.[2] Values (B.M.) for the complexes at room temperature are: $[Co(Me_3PO)_4](ClO_4)_2$, 4·56; $[Co(Me_3PS)_4](ClO_4)_2$, 4·31; $Co(Me_3PO)_2Cl_2$, 4·34; $Co(Me_3PS)_2Cl_2$, 4·32; $Co(Me_3PO)_2Br_2$, 4·46; $Co(Me_3PS)_2Br_2$, 4·41; $Co(Me_3PO)_2I_2$, 4·46; $Co(Me_3PS)_2I_2$, 4·42.

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